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Editor: EDWARD S. DANA.

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VOL. XXVI—[WHOLE NUMBER, CLXXVI.]

NEW HAVEN, CONNECTICUT.
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[FOURTH SERIES.]

Art. I.—*On the Emission of Electricity from the Induced Activity of Radium*; by William Duane.*

1. In the winter of 1905–1906, I made some experiments on the decay of the induced activity of radium, using as a means of measurement the quantity of electricity carried by the a and β rays instead of the ions produced by them. Up to that time this method of studying the decay curves had not been employed. A description of the experiments was presented at a meeting of scientists held at the University of Colorado in the spring of 1906, a brief résumé of which

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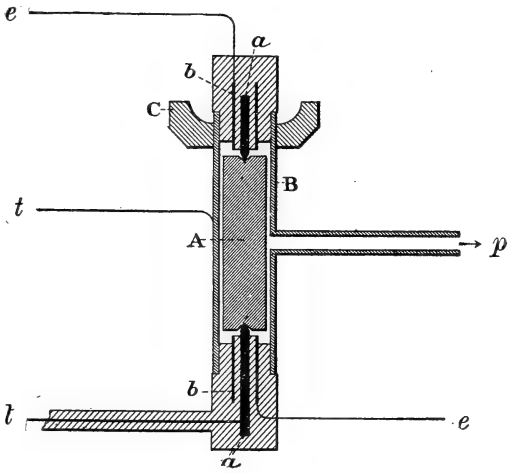

Connections: p, to pump; e, e, to earth; l, to electrometer; t, to battery.

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* Translation by the author of a paper published in "Le Radium" (vol. v, p. 65, March, 1908), entitled: Sur l'émission d'électricité par la radioactivité induite du radium.

appeared in Science.* Since then I have been able to repeat the experiments and carry the investigation somewhat further in the radium laboratory of the University of Paris. It gives me very great pleasure to thank Madame Curie and her assistants for their kindness to me during my researches.

2. Figure 1 represents the arrangement of the apparatus. *A* is a metallic cylindrical electrode, 11^{mm} long and $3{\cdot}42^{mm}$ in diameter, made radio-active by exposure to radium emanation. *B* is a tube of the same material as *A*, having an internal diameter of $4{\cdot}30^{mm}$. *A* can be held accurately in a position coaxial with *B* by the two metal points *aa*, and in this position there is everywhere a distance of only $\cdot 44^{mm}$ between the outer surface of *A* and the inner surface of *B*. The two metal points *aa* are imbedded in ebonite plugs, the upper point being completely insulated by the ebonite (in some experiments it formed one piece with *A*), and the lower one connected by suitably protected wires to a quadrant electrometer. The currents of electricity flowing toward or away from *A* were measured sometimes by the rate of change of the deflection of the electrometer, and sometimes with the aid of a piezo-electric quartz. The metal rings *bb*, connected to earth, served as guard rings to prevent currents from flowing between *A* and *B* along the surface of the ebonite.

3. The method of procedure was as follows: The electrode *A* was suspended by a pair of metal tweezers in radium emanation contained in a metal can for a period of at least 20 hours. It was charged during the period to a negative potential of 88 volts with respect to the can, thus insuring approximately saturation amounts of the induced activity. At the end of the period *A* and the ebonite plug were quickly placed in their positions in the tube *B*, and hot sealing wax poured into the cup *C* so as to form an air-tight joint between the plug and the tube. The air between *A* and *B* was then quickly exhausted. In the earlier experiments it was pumped out to a pressure of 1 or 2^{mm} of mercury by means of a mechanical oil pump, and then the residual air allowed to expand quickly into a glass globe previously exhausted to a good vacuum. In the later experiments, however, the exhaustion was accomplished by means of carbon cooled to the temperature of liquid air, the well-known Dewar method. After the vacuum had been produced the current flowing to or from *A* was measured at intervals of from two to five minutes, the tube *B* being at zero potential or charged by a battery positively or negatively. Usually the first satisfactory reading could be taken ten or twelve minutes after the electrode *A* had been withdrawn from the emanation.

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* Science, xxiv, pp. 48–49, 1906.

4. With the tube *B* connected to earth the electrometer always indicated a current flowing toward the electrode *A*, or, what would produce the same deflection, a discharge of negative electricity away from it. The current continued until the electrode became charged to a positive potential in the neighborhood of one volt, at which potential the discharge was apparently compensated by a flow in the opposite direction. A Volta electromotive force always acts between the tube *B* and the electrode *A*, even if they are of the same material. This electromotive force could be determined by reading the permanent deflection of the electrometer before exhaustion, when the space between *A* and *B* contained air. Usually the deflection indicated an electromotive force of about $\frac{1}{10}$th of a volt, and *always* one in such a direction as to oppose the current in the vacuum. Hence the observed discharge of electricity cannot be due to the Volta electromotive force. The electromotive force decreases with the time, but judging from some experiments I have made, it is not directly due (at least for the most part) to the deposit of radium A, B and C on the electrode. I have tried to obtain evidence for such a Volta effect, but have not succeeded.

5. The Volta electromotive force, however, alters the magnitude of the discharge, and for this reason in taking readings for the decay curves of the induced activity I adopted the usual method of charging the tube *B* successively to equal and opposite potentials. If *B* is charged to a positive potential of 1·5 volts or more, a current flows toward the electrode, and reversing the sign of the potential reverses the direction of the current. The current toward the electrode, however, is considerably larger than that away from it, the excess being due to the discharge of negative electricity from it.

6. Tables I and II contain several series of readings. The amounts of radium emanation used to make the electrode radio-active were those produced from 3 or 4^{mg} of $RaBr_2$ in one to five days. No attempt was made to collect all the induced activity on the electrode, and probably a large part of it settled on the tweezers that held the electrode in the emanation. Table I contains the results of experiments with an iron electrode and tube. In the first column the time after the electrode was removed from the emanation is tabulated, and in the second and third the currents to and from the electrode produced by potentials of $\pm 2{\cdot}2$ volts applied to the tube. First the current toward the electrode (called hereafter the positive current) was measured, then two minutes later the negative current and so on alternately. The corresponding columns of Table II contain similar results for a brass electrode and tube.

7. The same amount of emanation was not used in each case, so that the magnitudes of the currents in the two tables cannot be compared with each other; but it will be noticed that with brass surfaces the positive current is six times as large as the negative, whereas with iron surfaces it is only three times as large. Thus the nature of the surfaces has a considerable effect on the currents, a fact that was not unexpected, as undoubtedly the secondary and tertiary etc. rays from both surfaces furnish carriers for the electric charges.

TABLE I.

Iron Tube and Electrode

Time in min.	+Current mm./sec.	−Current mm./sec.	½ sum
11	5·00		1·64
13		1·68	
15	4·72		1·54
17		1·58	
19	4.43		1·45
21		1·49	
23	4·03		1·29
25		1·43	
27	3·86		1·23
29		1·39	
31	3·57		1·13
33		1·25	
35	3·16		0·96
37		1·20	
39	2·96		0·90
41		1·12	
43	2·78		0·84
45		1·10	
47	2·55		0·75
49		1·01	
51	2·45		0·74
53		0·93	
55	2·16		0·63
57		0·86	
59	1·98		0·57
61		0·81	
69	1·59		0·45
71		0·66	

TABLE II.

Brass Tube and Electrode

Time in min.	+Current mm./sec.	−Current mm./sec.	½ sum	+Current for 0 potential
12		2·27		
14	10·50		4·19	4·30
16		1·97		4·14
18	9·80		3·94	4·05
20		1·86		
22	9·35		3·77	
24		1·75		3·59
26	8·85		3·59	3·38
28		1·60		3·31
30	8·33		3·39	3·19
32		1.50		
34	7·64		3·08	2·80
36		1·45		
38	7·00		2·79	
40		1·39		2·48
42	6·30		2·46	
44		1·36		2·08
46	5·82		2·24	
48		1·31		
50	5·44		2·11	
52		1·13		
54	5·10		1·99	
56		1·10		1·70
58	4·65		1·79	
60		1·03		
62	4·20		1·62	1·51
70		0·78		
72	3·58		1·41	

8. The question whether any current is due to the ionization of the residual quantity of air left between the metal surfaces is an important one, and several series of experiments

were made to test this point. For instance, in one series the positive current measured with a liquid air vacuum was 3·04. On allowing air to enter the tube to a pressure (measured roughly by a small mercury manometer) of about 1·5^{mm} of mercury, the current six minutes later rose to 3·21. Six minutes later still the liquid air vacuum having been reproduced, the current fell to 2·34. Correcting for the decay of the current by taking the mean (2·69) of the first and last values, we see that the ionization in the air at 1·5^{mm} of pressure increases the current from 2·69 to 3·21, i. e., less than 20 per cent. A number of such experiments showed that the currents due to ionization in air between A and B at pressure of 1 to 2^{mm} were somewhat less than the currents to be measured, and it follows that the infinitesimal quantity of air left after exhaustion by the liquid air process can have no appreciable effect on the currents. This is to some extent due to the fact that the surfaces of the tube and electrode were very close together. In fact, the apparatus was designed to minimize the effect of ionization in the air as much as possible.

9. The fourth column in Tables I and II contains the values of ½ the algebraic sum of the positive and negative currents. This ½ algebraic sum represents roughly the discharge per second of negative electricity from the electrode in zero electric field less the negative electricity received by the electrode per second from the surface of the tube. Let e be the difference between these two currents, and $\pm i$ be the current produced by the applied electromotive force: i represents, then, the effect of the impressed electromotive force on the slow-moving electrons projected from the metallic surfaces. When the tube is charged positively, the positive current is

$$i_1 = e + i, \tag{1}$$

and when charged negatively, the negative current is

$$i_2 = e - i, \tag{2}$$

and evidently

$$e = \frac{i_1 + i_2}{2}$$

10. The above is the usual method of analyzing the currents in similar cases, but the theory contains two assumptions, first that the small electromotive force (2·2 volts) does not perceptibly change the value of e, and second that the current i has the same absolute magnitude whichever way the electromotive force acts. It is probable that neither of these assumptions is absolutely correct in the present case, but that the equations approximately agree with the facts may be seen from the following experiments.

11. The decay of the rate of discharge of electricity from the electrode with B put to earth was studied. For this purpose a zero method of measuring the currents is necessary, and the piezo-electric quartz was chosen, for in measuring currents by it the electrode is always held at zero potential. The currents measured by the quartz with B put to earth, but otherwise under the same conditions as before, appear in column 5 of Table II. These data represent a series of measurements distinct from that tabulated in columns 2 and 3. In order to reduce the readings to the same scale the positive currents under an electromotive force of 2·2 volts were measured several times, for instance at $t=22$, 36 and 64. With these values for comparison the measurements with the quartz were reduced to the same scale as the others. It will be noticed that the discharge current e for zero potential is with two exceptions some 10 per cent less than the $\frac{1}{2}$ algebraic sum of the currents tabulated in column 4. This difference is in part at least due to the Volta electromotive force, which, as I mentioned above, always acted in such a direction as to reduce the discharge of negative electricity from the electrode. From these experiments it appears that equations (1) and (2) are roughly correct.

12. We can, however, analyze the currents in other ways. We can, for instance, say that the currents are due to two streams of electricity s_1 and s_2 projected from the surfaces of the electrode and tube respectively; that when no electromotive force acts the current is

$$e = s_1 - s_2$$

and that when an electromotive force is applied one of the two streams, s_1 or s_2 is more or less checked. If Δs_1 and Δs_2 are the changes produced by the electromotive force, the positive and negative currents are

$$i_1 = s_1 - (s_2 - \Delta s_2) = s_1 - s_2 + \Delta s_2$$
$$i_2 = s_1 - \Delta s_1 - s_2 = s_1 - s_2 - \Delta s_1$$

If $\Delta s_1 > s_1 - s_2$, there would be a resultant current away from the electrode in the second case. Applying this theory to the data for the brass electrode, it appears that for 2·2 volts Δs_1 and Δs_2 must be some 50 per cent larger than $s_1 - s_2$; that is, there must be a large number of slow-moving β-particles projected from both surfaces, rays that 2 volts will stop. Such rays are produced by polonium,* radium† and other radio-active substances. The experiments further show that approximately $\Delta s_1 = \Delta s_2$ for the same electromotive force. The assumption made in this theory is that the value of s_1 does not depend on

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* J. J. Thomson, Nature, Dec. 15, 1904. Proc. Camb. Phil. Soc., xiii, Pt. 1, p. 39, 1905.

† E. Rutherford, Radio-activity, pp. 151–154.

that of s_2, and vice versa. As the secondary rays depend on the primary, and as there are tertiary rays depending on the secondary, etc., this assumption is probably not strictly correct.

Of course s_1 and s_2 may be further analyzed into their constituents α and β rays, secondary and tertiary, etc.

13. We now come to the important question, do the decay curves that can be drawn with the data in Tables I and II coincide with curves drawn from ordinary ionization data ? It will

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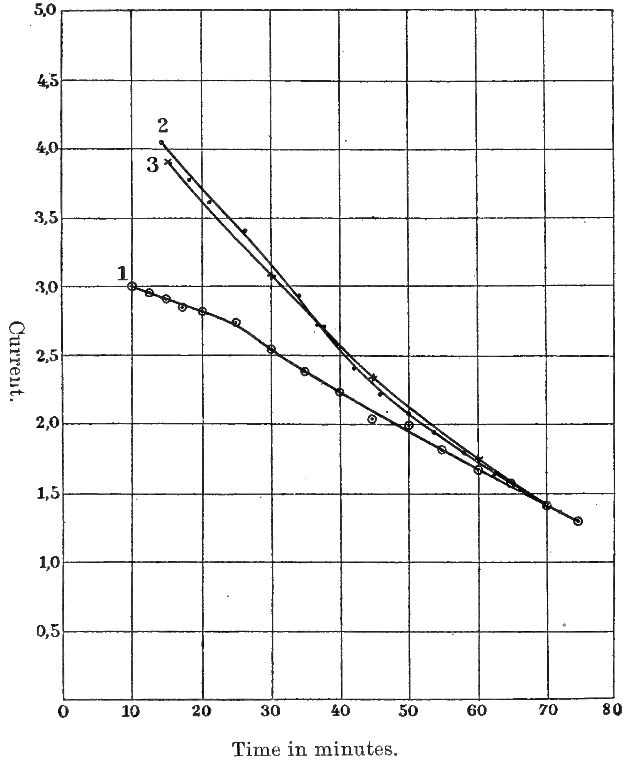

be seen that they do not. For comparison I measured the currents due to the ionization in air produced by the α rays, when the electrode was made active in exactly the same way as before. The electrode, after being withdrawn from the emanation, was placed opposite a hole in a large condenser, and the decay of the ionization current due to the α rays measured. Table III, column 2 contains the values of the currents measured by the piezo-electric quartz, and column 1 the time in minutes after the electrode had been withdrawn from the emanation. In order to compare them, I have drawn this curve and the curve representing the decay of the positive current for the brass surfaces (Table II, column 2) together in figure 2. Curve 1 represents the decay of the *a* ionization current in air at atmospheric pressure, and curve 2 that of the positive current in vacuum. The scales of the two curves were so chosen as to make them coincide at $t = 70$. It is easily seen that they do not coincide at other points, the curve representing the charge carried by the rays being much steeper than the other.

14. The explanation of this undoubtedly is that radium B, which under ordinary circumstances produces an almost inappreciable amount of ionization, does emit a very appreciable number of negatively charged rays. For the sake of comparison, I have calculated the theoretical curve that one should get under the supposition that radium B emits as much electricity during its change as radium C does during its. This is curve 3 in the figure. It is drawn under the assumption that there is on the electrode, to start with, equilibrium amounts of radium A, B and C, i. e., amounts that are inversely proportional to their respective decay constants, and that initially the quantity of radium B present emits as much electricity per second as does the quantity of C present. The scale of the theoretical curve was chosen so as to coincide with the others at $t = 70$, and it appears that the experimental curve 2 is a little steeper even than the theoretical one. In making the calculations I used constants corresponding to decay to half value in 3, 28 and 21 minutes respectively, for radium A, B and C. It is probable that the last two values, 28 and 21, are too high. Slightly smaller values would bring the theoretical curve closer to the experimental one.

All the curves that I have examined representing the positive currents and the $\frac{1}{2}$ algebraic sum of currents, are steeper than the theoretical curve. Curves representing negative currents are usually somewhat less steep than those representing positive currents, but lie much nearer curve 3 than curve 1. It follows that radium B must emit its full share of negative electricity when changing into C.

The theoretical curve representing radium C alone coincides so closely with curve 1 that I have not drawn it in the figure.

15. In some interesting experiments H. W. Smith* has shown that radium B produces a slight ionizing effect. He attributed the ionization to easily absorbed rays, probably β-rays. The ionization produced by rays from radium B can be shown very easily with the aid of the apparatus used in the

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* H. W. Schmidt, Physikal. Zeitschrift, vi, 897-903, 1905.

above described experiments. In one case the electrode *A* was made active exactly as before, placed in position in tube *B* and the currents measured at atmospheric pressure instead of in vacuum by means of the piezo-electric quartz. Column 3, Table III contains the results reduced to the same scale as those in column 2 for $t=70$. It appears that they by no means coincide except for $t=70$. In fact the data of column 3 represent points that would lie much more nearly on the theoretical curve 3 (figure 2) than on curve 1. This can be due only to the ionizing effect of radium B, and indicates that within a $\frac{1}{2}^{\mathrm{mm}}$ of the surface the rays from radium B produce ionization comparable with that produced there by the rays from radium C. This large ionization would be explained, if radium B produced *a* rays having a velocity just greater than the critical velocity required to produce ions. Such an hypothesis, however, is not absolutely required by the facts, and would contradict some results obtained by Bronson.*

TABLE III.

Time in minutes	Current in large con.	Current in small tube
10	3·01	4·15
12	2·97	
15	2·91	3·84
17	2·86	
20	2·83	3·53
25	2·76	3·30
30	2·54	3·09
35	2·38	2·89
40	2·26	2·64
45	2·04	
50	2·01	2·11
55	1·83	
60	1·70	1·80
65	1·58	1·59
70	1·42	1·42
75	1·31	

16. In order to estimate the velocity with which the carriers of electricity are projected from the metallic surfaces the brass electrode and tube were placed between the poles of an electromagnet and a magnetic field of 996 units produced parallel to their common axis. The currents were measured alternately with and without the field to correct for their decay during the experiments. The measurements indicate that both the positive and negative currents and also their algebraic sums are diminished by the magnetic field. According to the well-

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* Bronson, Phil, Mag. (6), xi, 806-812, 1906.

known formula for the radius R of the cylinder along the surface of which a β-particle moves in a magnetic field H,

$$R=\frac{m}{e}\frac{u}{H}$$

when u is the component velocity normal to the field, m the mass and e the charge of the particle. If any of the particles projected from one surface have velocities so small that R is less than $\frac{1}{2}$ the distance to the other surfaces, $0{\cdot}22^{mm}$ they will not reach the other surface. Further, some particles for which R is greater than this will be cut off also, by the field. Assuming that the ratio $\frac{e}{m}$ for the carriers of electricity is that of the electrons, namely $1{\cdot}87\times10^7$, the velocity for which $R=0{\cdot}022^{cm}$ is

$$u=HR\frac{e}{m}=4\times10^8$$

It follows that a considerable number of the electrons must have velocities near or less than 4×10^8.

17. The effect of increasing the electromotive force applied to the tube B was also studied, measurements being taken during a series alternately with 1·5 volts and voltages ranging up to 80 volts. It appears that both the positive and negative currents are considerably increased by increasing the electric field, and that, up to 40 volts at least, their algebraic sum is decreased. These results can be explained on the assumption that the currents are carried by the β-particles shot off from the surfaces. An electric field between the conductors stops some of them. To calculate the velocity that 40 volts would stop we have

$$\tfrac{1}{2}mu^2=40\times10^8e$$

or

$$u=3{\cdot}8\times10^8$$

It follows, as before, that a considerable number of the electrons must be projected with component velocities to the surfaces in the neighborhood or less than 4×10^8.

18. Combining the electric and magnetic effects we might calculate values for both $\frac{e}{m}$ and u, but owing to the complexity of the rays, and the difficulty of estimating just how many particles have velocities under a given limit, such estimates would not be worth much. The experiments show, however, that the order of magnitude of the effects are such as would be produced, if the currents were carried by β-particles, a considerable number of which had velocities normal to the surfaces in the neighborhood of 4×10^8 or less.

19. Experiments were made to measure the ratio between the charge carried by the rays from the induced activity and the charge carried by the maximum number of ions that can be produced in air by the same induced activity when all the α rays are absorbed in the air. As the latter is several thousand times the former, it is better to measure the ratio in two steps. In the first step, with the electrode A in the tube B, the ratio between the currents at atmospheric pressure and in a liquid air vacuum was measured, and in the second, with a smaller amount of activity, the ratio between the currents with the electrode in the tube, and in a larger condenser, was measured, both at atmospheric pressure. The product of the two ratios is the ratio required.

20. For the first step, the brass electrode having been made radio-active as before, it was placed in position in tube B and currents measured with the piezo-electric quartz at atmospheric pressure. Then the tube was rapidly exhausted by opening a stop-cock communicating with the reservoir containing carbon cooled to the temperature of liquid air, and the currents measured again. The electromotive force each time was 2·2 volts (i. e., 50 volts per cm.). The data appear in Table IV. Making the small corrections for the decay of the activity, we find for the ratio of the currents in air to that in vacuum, 61 for $t = 13$, and 69 for $t = 64$. Other experiments gave values ranging from 66 to 70 for 60 to 70 minutes after the electrode had been removed from the emanation. Earlier than this the ratio is smaller, owing undoubtedly to the fact that there is then proportionately more radium B on the electrode.

TABLE IV.

Time	Positive Current	
10	52·5	Atmospheric pressure
11	51·4	
13	0·82	Liquid air vacuum
14	0·78	
60	24·0	Atmospheric pressure
62	23·1	
64	0·322	Liquid air vacuum

21. To measure the ratio of the current in the tube B at atmospheric pressure and the saturation current when all the α rays produce ions in air, a large cylindrical condenser was constructed 19·8^{cm} long and 17·9^{cm} in diameter. A rod of brass suitably insulated held the electrode A at the center of the condenser, and at the same time acted as the electrode. A very much smaller amount of induced activity than before

having been deposited on *A*, the currents were measured first in the small tube and then in the large condenser, etc. One set of measurements is given in Table V. Making the correction for the decay of the activity, the ratio of the two currents at 62 minutes is 52·4. (The currents in the table are already corrected for a small ionization in the condenser before *A* was inserted.)

22. Combining this with the ratio previously determined, 69, we find that the saturation current in air when the a rays produce all the ions they can produce is 3,600 times as large as the positive current in the tube *B* in a liquid air vacuum, produced by the same activity. In these experiments the precaution was taken of sand-papering the end of electrode *A*, so as to remove all the activity deposited there.

TABLE V.

Time	+ Current	Electrode
55	9·45	in tube
62	425·	in condenser
63	425·	
70	7·00	in tube
71	6·95	

23. The total quantity of negative electricity emitted per second in vacuum from the electrode *A* is at least as great as the ½ algebraic sum of the positive and negative currents, and probably is greater than the positive current itself. The ratio of the positive current to this ½ algebraic sum is (for 2·2 volts) 2·5 for brass. Hence the negative electricity discharged per second from the electrode is at least as great as the $\frac{1}{3600\times 25} = \frac{1}{9000}$th part of the ionization current the a rays from its radio-activity are capable of producing. Rutherford* has found that each a particle projected from radium produces 86,000 ions. Assuming that each a particle from radium C produces a number of ions proportional to the length of its path and to the excess of its energy over the critical value, namely, 180,000 ions, it follows that for every a particle projected by radium C there are at least 20, and probably more than 50, electrons expelled from the active surface.

24. *Conclusions.* (*a*) A piece of metal made radio-active by immersion in radium emanation emits considerable quantities of negative electricity; and the rate of discharge decays with the time in such a way as to indicate that radium B when

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* Rutherford, Radio-activity, p. 434.

changing into C discharges as much electricity as does radium C when changing into D.

(*b*) A magnetic field parallel to the active surface stops part of the emission of electricity; and an electric field normal to the surface also alters the rate of discharge, the magnitude of the electric and magnetic effects being about what would be expected if the charge was carried by electrons, a considerable portion of which had component velocities normal to the active surface in the neighborhood of, or less than, $4\times10^8 \frac{\text{cm}}{\text{sec}}$.

(*c*) The total quantity of negative electricity emitted per second by an active brass surface is at least as large as the $\frac{1}{9000}$th part, and probably larger than the $\frac{1}{3600}$th part of the ionization current that can be obtained from the activity, if the a rays from radium C are completely absorbed in the air producing their maximum ionization; i. e., the number of ions produced by the a rays in air is less than 9,000 times, and probably less than 3,600 times the number of β-particles expelled from the wire during the same time. Assuming that each a particle from radium C can produce 180,000 ions, this means that for every a particle expelled from radium C, at least 20 and probably more than 50 electrons are emitted from an active brass surface.

(*d*) The number of ions produced by radium B in the air at atmospheric pressure close to (i. e. within ½ a mm. of) the active surface is comparable with the number of ions produced in the same space by radium C.

Radium Laboratory, University of Paris, 1908.

ART. II.—*Ilvaite from Shasta Co., California;* by BASIL PRESCOTT, Stanford University.

THE ilvaite described in this article occurs at Potter Creek, Shasta Co., California. The locality is well known to geologists on the Pacific coast, for it was from the caves in the Carboniferous limestone at this place that Dr. Merriam unearthed the Quaternary vertebrate remains,* and recently it has also attained some economic importance from the exploitation of the magnetite bodies that occur at the contact of this same limestone with an intrusion of diorite. It was during an examination of these ore deposits early in the present year that the writer noticed the presence of ilvaite.

Lindgren† has cited this mineral as a typical product of contact metamorphism, and the occurrence and association as seen in Potter Creek are in accord with this view. There were two occurrences noted. On both sides of a six-inch dike cutting through the limestone, a half-inch band of pure massive ilvaite was found, this, in places, sending out rough rectangular prisms into the limestone an inch or more in length. A few feet away, further search was rewarded by a number of ilvaite crystals associated with a coating of eroded quartz crystals on hedenbergite, a more common contact mineral. The crystals are about 7 to 8^{mm} in greatest dimension and are well formed, doubly terminated and symmetrical. The extremes in habit are shown in the figures, but even in the more elongated the prism zone is not as well developed as in the crystals from Elba.

Although the crystals are bright and untarnished, the signals were not distinct, and close measurements were impossible on account of vicinal faces and striations. The forms present are *m* (110), *s* (120), *b* (010), *o* (111), *r* (101), (890) (?) all of which are those more commonly developed in ilvaite with the exception of the doubtful new form (890) found on two crystals, where it replaces the prism *m* (110). The following measurements serve to identify the forms, the zone [*b*, *s*, *m*,] taken from one crystal, the zone [*o*, *r*,] from a second, as the two were not found measurable on the same crystal.

The most striking physical characteristics of the mineral as seen in this occurrence are the submetallic luster and greenish brown streak. The absence of limonite as an alteration product is noticeable. The cleavage is not prominent and neither the specific gravity nor the hardness would distinguish it from

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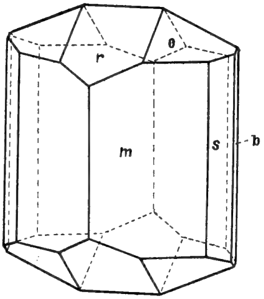
* Sinclair, Cal. Univ. Publ. Am. Arch. and Eth., vol. ii, pp. 1–27, 1904.

† Character and genesis of certain contact deposits. Trans. Amer. Inst. M. E., vol. xxxi, p. 227, 1901.

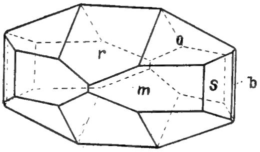
		Measured	Theoretical
$b \wedge s$	$(010 \wedge 120)$	36° 40′	36° 52′
$m \wedge s$	$(110 \wedge 120)$	20 09	19 27
$m \wedge m^{III}$	$(110 \wedge 1\bar{1}0)$	66 45	67 22
$o \wedge r$	$(111 \wedge 101)$	20 7	20 7
$o \wedge o^{III}$	$(111 \wedge 1\bar{1}1)$	40 28	40 15
	$(890 \wedge 120)$	16 15*	16 16

minerals of similar appearance. Before the blowpipe it fuses readily with slight intumesence to a magnetic globule, yields a small amount of water at high temperature in a closed tube and is readily soluble in hydrochloric acid, giving a gelatinous residue upon evaporation.

1



2



	Moss, Shasta Co., Cal.	Hillebrand,† Owyhee Co., Idaho	Hoffman,‡ Vancouver Island, B. C.	Theoretical
SiO_2	28·09	29·16	29·81	29·3
Al_2O_3	·32	·52	0·16	----
Fe_2O_3	20·80	20·40	18·89	19·6
FeO	29·93	29·14	32·50	35·2
MnO	3·24	5·15	2·22	----
CaO	15·89	13·02	13·82	13·7
MgO	·18	·15	·30	----
Na_2O	----	·08	----	----
Cr_2O_3	·13	----	----	----
H_2O	1·62	2·79	1·62	2·2
Total	100·20	100·41	99·32	100·00

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* This agreement is accidental, as the recorded value is the average of many readings on several faces.

† Bulletin U. S. G. S. No. 207, p. 45.

‡ Vol. 5, Annual Rep. Geol. Survey of Canada, 1889–90.

The material for the analysis given above was sorted from the massive ilvaite and all portions that might contain impurities or inclusions were carefully excluded. It was then submitted to H. R. Moss, whose results are tabulated (p. 15) with the two analyses available for America and with the theoretical for $HCaFe_2^{II} Fe^{III} Si_2O_9$, given by Dana in the sixth edition of the System of Mineralogy.

The material was air-dried at 95° C., and the total water obtained by a modification of Penfield's tube method. The only deviation from the usual course of analysis was in the determination of the manganese by triple precipitation as MnO_2 with bromine, in the filtrate from a basic acetate separation, and the subsequent precipitation of the chromium with ammonia.

Thanks are due Dr. A. F. Rogers, Stanford University, for advice and assistance in the preparation of this note.

ART. III.—*The Mechanics of Igneous Intrusion.** (Third Paper;) by REGINALD A. DALY, Massachusetts Institute of Technology, Boston.

Introduction.—In the April and August numbers of this Journal in the year 1903, the writer published papers outlining the hypothesis of magmatic stoping as explanatory of the rise of batholithic magmas in the earth's crust. The hypothesis had taken form in his mind after some ten years of perplexity as to the mode of intrusion which has actually characterized granite bodies. In Vermont, New Hampshire, British Columbia and other regions he had met with this urgent and important field-problem. Everywhere the facts derived from field observations were, in principle, the same; the method of intrusion seemed, for each batholith or stock, to be the same. Since the writing of the two papers the writer has studied in some detail a dozen other large batholiths and as many typical stocks occurring on the southern boundary of British Columbia. For all of these also the stoping hypothesis appears to afford the truest explanation of the mode of intrusion.

Quite independently Barrell arrived at a similar hypothesis, as he attacked, in 1901, the problem of the "Marysville batholith" in Montana. Unfortunately his monograph was delayed in publication until 1907, so that it is only quite recently that geologists have had the benefit of this brilliant and thorough study of intrusive mechanism.† Barlow and Coleman have noted their belief in the efficiency of stoping as an intrusive process.‡ At the other side of the world, Andrews has described the great intrusive masses of New South Wales,

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* Published by permission of the Commissioner for Canada, International Boundary Surveys.

† U. S. Geol. Surv., Prof. Paper No. 57, 1907.

‡ A. E. Barlow, Ann. Rep. Geol. Surv. of Canada, xiv, Part H, p. 79, 1904; A. P. Coleman, Jour. of Geol., xv, p. 773, 1907.

and most forcibly shows the value of the stoping hypothesis and of its implied principles in explaining the rocks and field-relations in that state.*

Notwithstanding the support given the hypothesis by the work of these and other observers, the main conception has not met with favor from many working geologists.† A number of objections have been raised, most of which were discussed in the first two papers of this series. Within the last five years an unusually large amount of experimental data has been added to the confessedly meager store of known facts concerning the physics of rocks and rock-melts. These laboratory results, when fairly interpreted, seem to the writer to dispose of most of the objections. Other objections fall away as soon as they are confronted with the indisputable, long-known facts concerning rocks and igneous magmas. A third class of the objections are more stubborn and still remain among the frank difficulties of the stoping hypothesis. It is, however, the writer's belief that these difficulties are small when compared to those adhering to the older theories of batholithic intrusion.

In this third paper some of the more significant, newer contributions of the experimental laboratory to the matter at issue will be noted and discussed. In the light of the whole body of fact as understood by the writer, he will attempt to make clear the reasons why the various criticisms against the stoping hypothesis do not seem fatal to its acceptance. Finally, a new statement of certain important corollaries and tests of the hypothesis will be offered. In their discussion a certain amount of speculation seems not only warranted but necessary. It is obvious that the basis of any theory of the igneous rocks must, in part, consist of speculative assumptions; for every fruitful theory must deal with the earth's invisible interior. Neither petrology nor geology can afford to leave the problem of the earth's interior "to the poets." The advances of modern chemistry have largely been made possible through constructive speculation as to the nature of molecule and atom; yet molecule and atom are as inaccessible as the core of the earth. In the nature of the case we can never hope to arrive at the final explanation of igneous-rock bodies without building and testing hypotheses of materials and processes in and under the earth's "crust." Not only petrology but, in marked degree, mining geology is awaiting a stable theory of batholithic intrusion, since upon it must largely depend sound petrogenic and minerogenic theory.

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* E. C. Andrews, Records, Geol. Surv., N. S. Wales, vii, Pt. 4, 1904, and viii, Pt. 1, 1905.

† Cf. Science, xxv, p. 620, 1907.

Like the first and second papers, this one does not present a complete discussion of the different topics. On another occasion the writer may publish a fuller statement of the favored solution of the complex problem.

Hypothesis of magmatic stoping.—The essential points are the following:

1. Each acid, batholithic magma has reached its present position in the earth's crust largely through the successive engulfment of suites of blocks broken out of the roof and walls of the batholith.
2. The blocks (xenoliths) are completely immersed in the magma, partly through the confluence of apophyses which have been injected on joints and other planes of weakness in the country-rock; more often the blocks represent the effect of shattering, due to the obviously unequal heating of the solid rock at magmatic contacts.
3. The sunken blocks must be dissolved in the depths of the original fluid, magmatic body, with the formation of a "syntectic,"* secondary magma.
4. The visible rock of each granite batholith or stock has resulted from the differentiation of a syntectic magma.

In applying the hypothesis to the explanation of actual field-occurrences other general considerations seem necessary. Stoping and abyssal assimilation on the batholithic scale are begun by a primary basaltic magma. This magma carries the heat required for the double action.† The source of the magma is to be found in a general basaltic substratum beneath the earth's solid crust. The crust is considered as composed of two shells. The lower shell is capable of injection by huge masses from the substratum, which retains open communication with the injected bodies. The latter are regarded as then stoping their way up into the overlying shell, in which the resulting derivatives of the syntectic magma are the visible batholithic granites and allied rocks.

These subsidiary elements of the problem here to be discussed have been described in the first intrusion paper and, more fully, in a later communication on "Abyssal Igneous Injection."‡ No one of these additional conceptions is essen-

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* This very convenient name for a magma rendered compound by assimilation or by the mixture of melts, has been proposed by F. Loewinson-Lessing, Comptes Rendus, 7^{e} session, Congrès géol. internat. St. Petersburg, 1899, p. 375.

† Whether the substratum is actually or only potentially fluid is not a vital question in this connection. T. J. J. See, as a result of his calculations, holds that the earth's interior may be fluid. He explains the observed rigidity of the planet as due not to its being a true solid but to the direct influence of gravity, which binds the earth-shells so effectively that bodily tides are almost wholly prevented. In any case rigidity and solidity are not synonymous terms. Cf. T. J. J. See, Astron. Nachrichten, v. clxxi, p. 378, 1906.

‡ This Journal, vol. xxii, 1906, p. 195.

tial to the idea of stoping *per se.* All of them may prove incorrect without invalidating the stoping hypothesis in its main feature. Combining them and the idea of stoping, the writer has constructed a general working hypothesis for the origin of the igneous rocks. It seems, therefore, expedient in the present paper to discuss the problem in its larger aspect.

Field Relations of the typical batholith.—A principal fact on which the stoping hypothesis is based has been amply illustrated in the published descriptions of granite stocks and batholiths. Most, if not all, of these bodies in their accessible portions have replaced nearly equivalent volumes of the respective country-rocks. They are generally cross-cutting bodies. Their roofs are rough domes or arches, from which large masses of the invaded rocks are sometimes pendant into the crystallized granite. In each of many cases erosion has destroyed much of the roof, and the roof-pendants, still preserving the regional strike of their structure-planes, are to-day exposed in section at the erosion-surface. Between the pendants and between the main walls of a large batholith, hundreds of cubic kilometers of country-rock formations are plainly missing; their place has just as plainly been taken by the granite.

A second principal fact is that, so far as granite batholiths and stocks are known, each of these bodies shows a cross-section enlarging with depth.* No one of them has yet exhibited a floor composed of older formations. In relation to visible country-rocks, all of them may be classed as subjacent, rather than as injected, bodies. In relation to the wall-rocks ten or more kilometers below the earth's surface, each batholith may have been truly injected as a kind of gigantic dike, but of this there is no direct proof. The actual observations in the field show unequivocally that the batholithic magmas have worked their way up by replacing and absorbing the country-rocks through the last few kilometers of ascent. Batholiths are not laccoliths.

A third generally observed fact is worthy of special attention. Where erosion has been profound the ground-plan section of the typical stock or batholith is seen to be elliptical and the profile-sections, as already noted, show that the upper-contact surface of the intrusive is dome-shaped. Both in ground-plan and in vertical sections the contact-surface is relatively smooth. Apophysal offshoots do interrupt the wall-rock, but the main-contact lines as mapped on ordinary geological maps are characteristically flowing lines. Large-scale,

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*See the numerous sections of stocks and batholiths in Lepsius' "Geologie von Deutschland"; also Barrell's monograph cited, and the writer's paper on the Okanagan Composite Batholith, Bull. Geol. Soc. America, xvii, p. 330, 1906.

angular projections of country-rock into a well uncovered batholith are comparatively rare. Such smoothness of main-contact surfaces is that which is to be expected on the stoping hypothesis. A projection of country-rock would suffer specially intense shattering by the magma, which would thus tend to destroy the projection and smoothen the wall of contact. The case is analogous to the familiar exfoliation on sculptured stone in great city fires; architrave, sill, abacus and plinth lose their corners, ornaments in high relief are rifted off, and flutings are effaced. Bowlders of disintegration through weathering furnish other analogies.

In detail of form as in the larger field-relations of the typical stock and batholith, therefore, we seem to have cumulative evidence in favor of the theory of replacement and especially in favor of the hypothesis of mechanical replacement. On the other hand, the more intimate becomes our knowledge of these field-relations, the more improbable the "laccolithic theory" becomes. Neither smooth, flowing contact-surfaces against a heterogeneous terrane, nor a general elliptical ground-plan, nor an invariable downward enlargement are expected to characterize a batholith if it is simply a huge laccolith.

These summary statements are founded on the writer's field-experience, and on a tolerably wide study of the geological literature relating to granitic intrusions. The essential idea of replacement rather than displacement is far from new; it has been a lasting merit in the able work of Barrois, Michel Lévy, Lacroix and others, that they have persistently held to this fundamental fact of field-occurrence. Yet there are to-day many working geologists who just as persistently refuse to recognize the fact of the field. The chief reason for this refusal has undoubtedly been that the replacement of the country-rocks has, until recently, been attributed to their progressive solution on the main contacts—in other words, to marginal assimilation. The patent difficulties of this one view have prevented many, perhaps most, geologists from subscribing to the conclusions of their French colleagues. The proved insufficiency of the marginal-assimilation hypothesis has thus discouraged belief in that kind of replacement, but it by no means alters the fact of magmatic replacement. On the other hand, this fact will stand, no matter what theories of intrusion may prevail.

So far as recorded, the stoping hypothesis is the only one which recognizes the progressive assimilation of country-rocks as the magma rises in the crust, and, at the same time, explains the common lack of chemical sympathy between granites and their respective wall-rocks. By this hypothesis the preparation of the upper and visible part of the magmatic chamber is largely a mechanical process, working along main contacts; the solution of the engulfed blocks is effected far down in the depths of the magma—by abyssal assimilation. The resulting syntectic magma may thus be in strong chemical contrast with the adjacent wall-rock at any one level. Marginal assimilation is not excluded but is considered as an accessory and subordinate phase in the act of replacement.

Contact-shattering.—It has been objected that rocks are good conductors of heat and that, therefore, strong temperature differences with resulting rending strains are not to be expected in the shell of country-rock immediately surrounding a batholithic magma. This objection has been recently made by an expert physicist now specially engaged on petrological problems, and evidently needs consideration.* The following table of coefficients of absolute conductivity seems, however, to show, on the contrary, that rock-matter is far from being ranked as a good conductor. The table has peen made by compiling the values noted in the Landolt-Börnstein's Physikalisch-chemische Tabellen (1905 edition) and in Winkelmann's Handbuch der Physik. The values for the rocks are of the order expected in view of the familiar proofs of the extremely slow cooling of lava-flows.†

	k
Silver, about	1·0000
Copper, "	·9480
Lead	·0836
Quartz	·0158
Marble	·00817
Granite	·00757 –·00975
Gneiss	·000578–·00817
Sandstone	·00304 –·00814
Basalt	·00673
Syenite	·00442
Glass	·00108 –·00227
Water, about	·00130
Paper	·00031
Flannel	·00023
Silk	·00022
Cork	·00013
Feathers	·0000574

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* Cf. A. L. Day, Science, xxv, p. 620, 1907.

† The steepness of the possible temperature gradient in the wall-rock is shown by the fact that, a few days after lava ceases flowing, one can walk on its crust, although the lava just below is at red heat (700°–950° C.) or is yet hotter. For many hours or for several days the gradient at the surface may equal or surpass 500° C. per foot.

In the manufacture of calcium-carbide a mixture of limestone and coke is submitted to the action of a powerful electric arc. At the end of a furnace-run (about fourteen hours in the plant at Ottawa, Canada) the flow of heat is nearly steady and the temperature gradient in the furnace is about 3000° C. per foot. In this case the diffusivity of the limestone-coke mixture in the interior of the thoroughly heated furnace must be well below 60 in the Kelvin system of units.

Weber has found that k for gneiss at 0° C. is 0·000578 and at 100° C. 0·000416, showing a very great lowering with increase of temperature.* In fact, through the interval 0°–100° C., k seems to vary about inversely as the absolute temperature.† If this law should hold to 1100° C. the conductivity of average rock at 1100° falls to about 0·001—nearly the value for water, which is famous as a poor conductor.

In the present connection the thermal diffusivity (κ) of rock, rather than its conductivity, is of first importance. If s = specific heat and d = density, we have

$$\kappa = \frac{k}{s.d}$$

For rock at room temperature (20° C.) Kelvin assumed 400 as the value of κ when the unit of length is a foot, the unit of time a year, and the unit of temperature one degree Fahrenheit. This value is close to that which represents the average of the determinations made for different rocks at room temperatures, during the years since Kelvin wrote his famous essay.‡

If κ be assumed as 400 at all temperatures up to 1300° C., it is possible to calculate the temperature gradient in the wall-rock of a molten batholith at the end of specified periods of time. For practical purposes the surface of contact may be regarded as infinite; let it further be considered as plane. Under these conditions the following Fourier equation furnishes the datum for calculating the temperature at a point x feet from the contact at the end of t years.§ In the equation b = the temperature of the magma; c = the temperature of the wall-rock assumed as initially uniform; and u = the required temperature. We have:—

$$u = b + (c - b)\,\frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{\kappa t}}} e^{-\beta^2}\,d\beta.$$

For values of $\frac{x}{2\sqrt{\kappa t}}$ which are less than 2·6 the value of the integral can be readily found from the table of the probability integral which appears in standard text-books on the Method of

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* Values taken from Landolt-Börnstein Phys.-Chemische Tabellen. Forbes and Hall have proved analogous relations for iron and for magnesium oxide; cf. J. D. Forbes, Trans. Roy. Soc. Edinburgh, xxiv, p. 105, 1867, and E. H. Hall and others. Proc. Amer. Acad. Arts and Sciences, xlii, p. 597, 1907.

† Cf. P. G. Tait, Recent Advances in Physical Science, 2d ed., London, p. 270, 1876.

‡ Trans. Roy. Soc. Edinburgh, 1862.

§ Cf. W. E. Byerly's Elementary Treatise on Fourier's Series, Boston, 1893, p. 86.

Least Squares. For higher values of $\frac{x}{2\sqrt{\kappa t}}$ the value of the integral can, in many cases, be computed by developing it into a series. Kelvin's value for κ is peculiarly favorable for such computation and the corresponding units have been used by the writer in the calculations.

Let b = 2200° F. (about 1200° C.); c = 400° F. (about 200° C.); t = 1, 4, 16, and 100 years; and let x have the different values shown in the left-hand column of the following table (I) The corresponding temperatures are shown in the other columns.

TABLE I.—Showing values of u when $\kappa = 400$ and

x	$t = 1$ year.	$t = 4$ years.	$t = 16$ years.	$t = 100$ years
0′	2200° F.	2200° F.	2200° F.	2200° F.
10′	1703	1947	2074	
20′	1263	1703	1947	
40′	683	1263	1703	
80′	408 5	683	1263	
100′	ca.400	537	1078	1703
160′	400	408·5	683	
200′	400	ca.400	537	1263
320′	400	400	408.5	
400′	400	400	ca.400	683

The table shows that, at the end of the first year, the temperature of the rock is but slightly affected by the magmatic heat at a point 80 feet from the contact, and that the temperature gradient for the 80-foot shell then averages nearly 23° F. per foot. At the end of four years the temperature is but slightly affected at a point 160 feet from the contact and the temperature-gradient is about 11° F. per foot.

But κ cannot be nearly so great as 400 in the case before us. We have seen that k decreases rapidly with rise of temperature in rock. The experiments of Weber, Bartoli, Roberts-Austen and Rücker, and Barus show that the specific heat of rock averages about ·180 at 20° C. and increases regularly with rise of temperature, so that at 1100° C. the specific heat averages about ·280.* It follows that thermal diffusivity in rock decreases with rising temperature even faster than the conductivity decreases. At 1100° C., κ may, indeed, be only

$$\left(\frac{\cdot 180}{\cdot 280} \times \frac{293}{1373} \times \frac{1\cdot 000}{\cdot 973} = \right) 0\cdot 141$$

or less than one-seventh, of the diffusivity at 20° C. For rock heated to 1000° or 1200° C. κ is, thus, probably not much more than 60 in the Kelvin system of units.

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*For references see J. H. L. Vogt, Christiania Videnskabs-Selskabets Skrifter, I. math.-naturv. Klasse, No. 1, p. 40, 1904.

It seems safe to assume, first, that the diffusivity of the gradually heated wall-rock may vary from 275 or less to 100 or 150; secondly, that the average diffusivity of an 80-foot shell heated during the first year by adjacent molten magma, will be no greater than 200. If κ be regarded as averaging 200 for all periods greater than one year, the four columns showing values of u in the table will serve if t is, respectively, 2, 8, 32 and 200 years.

As a result of somewhat rigorous calculation, then, it appears certain that the heating of wall-rock by plutonic magma must progress with great slowness and that the resulting temperature gradient in the shell adjoining the molten magma must be steep for many years after the original establishment of the contact.*

Further, Less has proved that rocks have highly variable coefficients of conductivity, some species possessing coefficients twice as high as those of other species.† It is also well known that bedded or schistose rocks conduct heat along and across their structure-planes at quite different rates. Where, therefore, the wall-rocks about a batholithic mass are heterogeneous, the heat-conduction is variable and expansional stresses must ensue.

A rough calculation of the enormous stresses involved in all these processes of differential heating was published in the second paper of this series, where also an account is given of the practical use which has been made of such stresses in primitive quarrying.‡ Every great city conflagration leaves manifold evidences of the shattering effects of the one-sided heating of a rock-mass—in columns, sills, and cornices of granite or sandstone.

There seems, therefore, to be a sheer necessity for believing in contact-shattering through differential heating and expansion in the thin shell of a country-rock which encloses a large body of molten magma. The evidence for the shattering is often exceedingly full and clear in the field. The broad or narrow belts of xenoliths so often found just inside the main contacts of batholiths are very hard to explain if those batholiths are due to laccolithic injection. The blocks are characteristically angular; they are generally not arranged with their longer axes parallel, as if they had been pulled off from the

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* By using the same Fourier equation it is not difficult to show that the loss of thermal energy which a magma suffers by conduction into the country-rock is relatively small, even after the lapse of two or three hundred thousand years. The long duration of the magmatic period in a slightly superheated plutonic mass of large size becomes easily understood.

† Phil. Trans., vol. clxxxiii A, p. 481, 1892.

‡ This Journal, xvi, p. 112, 1903; cf. Ann. Rep. State Geologist of New Jersey, 1906, p. 17.

walls by the friction of the moving magma. On the laccolithic theory one would expect many of the xenoliths to form elongated smears in the granite rock. This is indeed occasionally seen but most exceptionally; as a rule the xenoliths have just that irregularity of form and arrangement which they should have if they had been shattered off by the hot magma just before its final consolidation. Throughout its long, earlier history the magma must, in every case, have had a much more effective shattering power.

It may be noted that the shattering of crystals and rock-fragments, when immersed in silicate melts, has often been observed.* The strains are, in such cases, necessarily of a lower order than those developed on the wall of a batholith where, therefore, shattering is even more certainly brought about.

Relative densities of magma and xenolith.—In his first intrusion-paper, the writer published the results of his attempt to calculate the possible specific gravities of the chief types of molten magmas under plutonic conditions. The calculations were based on Barus's well-known fusion experiments on diabase. The specimen investigated had a specific gravity of 3·0178; when fused to a glass and cooled to 20° C., a specific gravity of 2·717. He further states that the glass† showed an expansion of 3·9 per cent in "melting" and, as glass, expanded 0·000025 in volume for a temperature rise of 1° C. through the interval 0°–1000° C. and 0·000047 in volume for 1° C. through the interval 1100°–1500°. The "melting" expansion (solidification-contraction) and the varying rate of expansion (or contraction) above and below 1000° C. seem to show that some crystallization of the melt took place during the experiment. Such crystallization was inevitable under the conditions of the experiment, in which the cooling lasted several hours. Barus's curves do not, therefore, show directly the volume changes suffered by pure diabase glass in passing from the molten isotropic state to the rigid isotropic state at room temperature. Excluding the "solidification" contraction, the glass loses but 3·5 per cent of its volume in passing from the molten state at 1400° C. to room temperature; the loss of volume through the same temperature interval was calculated in the first paper as about 8 per cent. Barus found that the net decrease in specific gravity in passing from rock at 20 C. to glass at 20° C. was 10 per cent. For his diabase specimen, therefore, the decrease of specific gravity in passing

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* Cf. C. Doelter and E. Hussak, Neues Jahrb. für Min. etc., 1884, p. 18; A. Becker, Zeitschr. d. d. geol. Ges., xxxiii, p. 62, 1881.

† "Throughout this paper the molten rock solidifies into an obsidian." C. Barus in Bull. 103, U. S. Geol. Surv., p. 26, 1893.

from 20° C. to molten condition at 1200° C. is possibly only about 13 per cent, instead of about 16 per cent, as noted in the first paper.*

Quite recently J. A. Douglas has made a number of very careful measurements of the densities of typical igneous rocks and of their respective glasses, all specific gravities being taken at room temperatures.† Douglas's method is reliable and his results accordant. For gabbro he found the decrease of specific gravity, in passing from rock to glass, to be 5·07 per cent. Delesse had found the decrease to be 11·46 per cent, as the average of measurements of two specimens from different localities Barus's determination, 10 per cent, is intermediate between the two.

It seems probable, therefore, that a decrease of 6 per cent in specific gravity (rock to glass at 20° C.) is close to the minimum for the average gabbroid rock, and it is possible that Barus's 10 per cent decrease is too high for average gabbro. For present purposes it is safer to use the minimum value of 6 per cent. Similar minima for diorite (6 per cent), quartz diorite and tonalite (7 per cent), syenite (8 per cent) and granite (9 per cent) have been estimated from the numerous measurements of Delesse, Cossa and Douglas. Each of these rocks certainly

Table II.

	Specific gravity of Crystalline rock at			Specific gravity of same rock when molten at			
	20°C.	1000°C.	1300°C.	1000°C.	1100°C.	1200°C.	1300°C.
Gabbro and diorite	2·80	2·73	2·71	2·57	2·56	2·54	2·53
	2·90	2·83	2·80	2·66	2·65	2·64	2·63
	3·00	2·92	2·90	2·75	2·74	2·73	2·72
	3·10	3·02	3·00	2·84	2·83	2·81	2·80
	3·20	3·12	3·10	2·94	2·92	2·91	2·91
Quartz-diorite and tonalite	2·70	2·63	2·61	2·46	2·45	2·44	2·43
	2·80	2·73	2·71	2·54	2·53	2·51	2·51
Syenite	2·60	2·54	2·52	2·33	2·32	2·31	2·31
	2·70	2·63	2·61	2·42	2·41	2·40	2·40
	2·80	2·73	2·71	2·52	2·51	2·50	2·50
Granite and gneiss	2·60	2·54	2·52	2·31	2·30	2·29	2·29
	2·70	2·63	2·61	2·40	2·39	2·39	2·38
	2·80	2·73	2·71	2·49	2·48	2·47	2·47

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* Bischof, in 1841, found that basalt expanded 7 per cent in passing to a glass at room temperature, and 10·4 per cent in becoming molten. (Quoted from Zirkel's Lehrbuch der Petrographie, 2d ed., 1893, vol. i, p. 683.)

† Quart. Jour. Geol. Soc., xiii, p. 145, 1907.

expands in the interval 20°–1300° C. as much as 0·000025 volume per degree Centigrade (Barus and Reade—see first paper). This average may safely be employed as a means of determining the minimum decrease of density which each rock-type undergoes in passing into the molten condition. On this basis the writer has constructed the preceding table (II), which shows the changes of specific gravity at convenient temperature intervals.

Table III shows the changes in specific gravity undergone by blocks of stratified and schistose rocks (common country-rocks about batholiths), as these blocks assume the temperature (1300° C.) of molten magma in which they are immersed.

TABLE III.

	Range of sp. gr. at 20°C.	Range of sp. gr. at 1300°C. (solid)
Gneiss	2·60–2·80	2·52–2·71
Mica schists	2·75–3·10	2·67–3·00
Sandstone	2·20–2·75	2·13–2·67
Argillites	2·40–2·80	2·32–2·71
Limestone	2·65–2·80	2·57–2·71

It appears from these tables that nearly all xenoliths must sink in any molten granite or syenite; most xenoliths must sink in molten quartz-diorite, tonalite or acid gabbro. Many xenoliths might float on basic gabbro but the heavier schists and gneisses must sink in even very dense gabbro magmas at 1300° C.

Giving, then, the highest permissible values to the specific gravities of magmas, it is still true that blocks, such as are shattered from the wall or roof of a batholith, must sink when immersed in most magmas at atmospheric pressure. As shown in the first intrusion paper, the blocks would likewise sink, though the magma enveloping them lies at depths of ten or fifteen kilometers below the earth's surface.

Sinking of the shattered blocks.—It has been objected to the stoping hypothesis that the viscosity of granitic magmas is too great to allow of the sinking of blocks even much denser than those magmas.* This objection has, however, never been sustained by definite experimental or field proofs. The xenoliths visible along batholithic contacts have assuredly not sunk far from their former positions in wall or roof and the reason for this must be sought in the high viscosity of the magma. High viscosity is an essential attribute of a nearly frozen magma. The phenomena of fractional crystallization and of magmatic differentiation unquestionably show that each

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* Cf. W. Cross, G. F. Becker, and A. L. Day, Science, xxv, p. 620, 1907.

plutonic magma must pass through a long period of mobility. The most viscous of granitic magmas, the rhyolitic, issues at the earth's surface with such fluidity that the rhyolite often covers many square miles with a single thin sheet. The absolute viscosity of the Yellowstone Park rhyolites must have been of a low order when many of these persistent flows were erupted.*

Even granting that the kinetic viscosity of a plutonic magma is thousands of times that of water, it seems inevitable that it could not support xenoliths more dense than itself. In a few days or weeks stones will sink through, and corks will rise through, a mass of pitch, the viscosity of which is more than a million of millions of times that of water.† Ladenburg has lately shown that small steel spheres will, in a few minutes, sink through twenty centimeters of Venetian turpentine, a substance 100,000 times as viscous as water.‡ Ladenburg's experiments have verified the generally accepted equation expressing the rate of sinking of a sphere in a strongly viscous fluid:

$$x = \frac{2}{9} \frac{gr^2 (d - d')}{v}$$

were x = the velocity of the sphere when the motion is steady; g = the acceleration of gravity; d = the density of the sphere; d' = the density of the fluid; r = the radius of the sphere; and v = the viscosity of the fluid.§ The equation shows that the velocity of sinking varies directly as the square of the radius of the sphere. This fact may be correlated with the observation so often to be made on granite contacts, that large xenoliths are rare. This apparently means that, at the end of the shatter-period, the viscosity is truly so high as to allow of the smaller blocks being trapped at high levels in the freezing magma, while the large blocks, with greater velocity, shall have sunk into the depths.

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* See Atlas accompanying Monograph 32 of the U. S. Geol. Survey. King described the great rhyolite flows of Nevada as bearing "abundant evidence of true fluidity at the period of ejection." U. S. Geol. Explor. 40th Parallel. Sys. Geol. 1878, p. 616.

Doelter has studied the behavior of a large number of crystalline rocks and minerals during fusion. His results show that the temperature-interval between the stage of softening and that of notable fluidity averages, for the basic rocks, about 50° C., and for the acid rocks, about 90° C. (Tscher. Min. u. Petrogr. Mitth. xx, p. 210, 1901.) The interval is not great and it certainly seems unsafe to deny that even the most viscous, because cooled, lavas were fluid in depth.

† Jamin et Bouty, Cours de Physique, tome I, 2e fascicule, Paris 1888, p. 135; cf. Daniell's Text-book of the Principles of Physics, 2d ed., London, 1885, p. 211.

‡ Annalen der Physik, xxii, p. 287, 1907.

§ Poynting and Thomson, Text-book of Physics, Properties of Matter. London, p. 222, 1902.

Doelter estimates that the pressure of from 7500 to 11,000 meters of rocks increases magmatic viscosity no more than 20 to 30 per cent.* If the increment be anywhere near this value we may be certain that the viscosity of superheated, plutonic magma is relatively low. Becker has calculated that the viscosity of a Hawaiian basaltic flow, not one of the most fluid, was, at eruption, about fifty times that of water. The more fluid rhyolite flows may have viscosity a thousand times greater than that of water. The corresponding viscosities of the same magmas when ten kilometers underground may, then, be possibly no more than from sixty to fifteen hundred times that of water. One must conclude that a xenolith, even very slightly denser than such a plutonic magma, must sink into it. Since such magmas necessarily cool with extreme slowness, there is evidently good ground for believing that an enormous amount of solid rock could be engulfed before practical rigidity is established. The average xenolith must sink in a less dense magma with the viscosity of pitch—yet how much more rapidly in magma possessing the low viscosity which is postulated in any of the ruling theories of plutonic-rock genesis!

Problem of the cover.—The stoping hypothesis presents an obvious principal difficulty; it refers to the apparent danger of the foundering of the roofs covering the larger batholiths. Under plutonic conditions (at depths of from three to ten kilometers) the average molten granite would have a specific gravity no higher than 2·40. The average rock of its roof has a specific gravity of about 2·70. If, then, through orogenic movement, a large mass of the roof-rock became once wholly immersed in the granite, it would not only founder itself but through subsequent buckling the whole roof might collapse and founder in sections. Such a catastrophe has almost certainly not happened in the case of any Paleozoic or later batholithic intrusion. This difficulty has been emphasized by Barrell, who has justly given it a prominent place in his monograph.† Lawson speaks of batholiths 100 miles in diameter and also finds the necessity of explaining their roof-support as a principal ground of unfavorable criticism.‡

The present writer cannot claim to have solved this problem, but he does not find it to form a fatal objection to the hypothesis. In the first place, it seems clear that all the other hypotheses of granitic intrusion are facing the same dilemma. All of them expressly or tacitly postulate some degree of fluidity in each granitic mass as it either replaces or displaces

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* Physikalisch-chemische Mineralogie, Leipzig, p. 110, 1905.

† Op. cit., p. 172.

‡ Science, xxv, p. 620, 1907.

its country-rocks. We have seen that, though the viscosity of such a magma may be several hundred times that of water, the roof-sections, once immersed, must sink in the magma. All petrologists who believe in magmatic or other differentiation as operative in batholiths must face the common difficulty.

Secondly, the writer has shown reasons for believing that the earth's crust at present rests on a continuous *couche* of basaltic (gabbroid) magma, either quite fluid or ready to become fluid when injected into the crust. If the average specific gravity of the crust is 2·75 (a probable value), it would as a whole be quite able to float on the basaltic *couche*, which, as noted in Table II, would probably have a specific gravity over 2·90. Imperfect as the numerical data are, we seem justified in concluding that the earth's crust is now, as a whole, in stable flotation.*

It may have been entirely different in pre-Keewatin (earliest Archean) time when the superficial, acid *couche* of the primitive earth began to solidify. Then foundering may have taken place, as Kelvin imagined, and the early formed crusts could have sunk a score of kilometers or more until they met the denser *couche* below. Possibly some of the complexity of the pre-Cambrian formation may be referable to this unstable condition of the early crust. Already in Keewatin times the acid shell was solidified and was then penetrated by basaltic injections which reached the surface, forming the heavy masses of greenstones belonging to that period. Since then the crust has remained essentially coherent, and through it the primary basalt has, at many times and places, been erupted. It is, however, quite possible that the lack of system among the axes of the Laurentian batholiths and the abundance of those batholiths are both explained by the thinness and weakness of the crust in post-Keewatin and pre-Cambrian time.

For Paleozoic and later batholiths there is a well-defined law that they have penetrated the crust only on the sites of folded geosynclinals, and that the larger batholithic axes are usually arranged parallel to the respective geosynclinal and mountain-range axes.

In other words, the intrusion-history of the globe may be conceived as divisible into three epochs: the first being that in which the outer primary shell was becoming stable through successive solidifications and founderings; the second being the post-Keewatin (Laurentian) epoch of very general interaction between the fluid basaltic substratum and acid crust, without extensive founderings but with development of many large, irregularly occurring batholiths; the third, a period of the localization of batholiths in certain mountain-built belts,

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* For a further discussion of this point see this Journal, xxii, p. 201, 1906.

where alone there seems, in this third period, to have occurred the injection of molten magma in masses of batholithic size—in no known case accompanied by wholesale foundering.

Again, granting the hypothesis that a visible post-Archean batholith is the acidified, upper portion of a basaltic body originally injected to a level less than about ten or fifteen kilometers from the earth's surface (perhaps the level of no strain), it is not difficult to see that extensive foundering may be impossible. Only after some differentiation or acidification of the primary magma would any part of it become less dense than the average roof-rock. Xenoliths of the heavier gneisses and schists would, however, sink. When dissolved in the primary magma their material—added to that dissolved along the main contact-surfaces—would lower the density and inaugurate the stage of general stoping. Only when the resulting syntectic magma has been formed in large amount is there any danger of roof-foundering. But it is evident that, in the process of dissolving the engulfed blocks, the magma is losing heat. In every post-Archean batholith the magma, because of exhaustion of the heat-supply, seems to have been arrested in its upward course at average distances of one or more kilometers from the earth's surface. The syntectic magma, less dense than the roof-rock, is thus necessarily of limited depth. That depth represents the thickness of the *couche* which endangers the stability of the roof. If, now, we imagine the buckling of the roof with the complete immersion and sinking of certain parts of it, the foundering must be limited by the width of the injected body (seldom over fifty kilometers) and by the thickness of the acid *couche* (ten kilometers or less). Extensive floods of rhyolite and allied rocks may have issued at the surface in consequence of partial foundering (faulting), but great crustal catastrophes involving large areas would not be expected.

Finally, it should be noted that post-Archean granitic intrusions have regularly followed periods of prolonged orogenic crushing, during which accumulated tangential stresses are effectually relieved. As the magmas work their way up into the folded terranes there is relatively little chance for the buckling of the roof. Until it is buckled and immersed in the magma it cannot sink. Now the heat of the magma, though it shatters the roof-rock at the immediate contact of solid and fluid, must tend to expand the roof, tighten it, prevent normal faulting and so strengthen the roof. The cover of the batholith is thereby kept in an exceptionally rigid condition. Its strength is, initially, that of a domed shell spanning diameters not very many times the thickness of the shell. The strength is increased, as with the groined roofs and arches of Gothic architecture, by the presence of roof-pendants; and by thermal expansion, the whole is strongly knit together. Immersion and foundering of roof-sections may, therefore, not have been possible in the case of post-Archean batholith or stock.

In spite of the highly theoretical nature of some of the foregoing argument, it appears to the writer to carry weight enough to warrant our regarding the difficulty in question as not destructive of the stoping hypothesis. The problem needs further study in connection with this and all other conceptions of granitic intrusion.

Supply of the necessary heat; magmatic superheat and its causes.—Whether the observed average temperature gradient within the earth's crust is to be explained as due to original heat (inherited from an early epoch in the development of the earth either from a gaseous or planetesimal nebula), or whether the gradient is due to the evolution of heat with the break-up of radium and other radio-active substances, are general questions not immediately affecting the stoping hypothesis. We need go no further back in the thermal problem than to secure an estimate of the minimum temperature of the primary magma when abyssally injected and thus prepared for stoping and assimilation. This estimate is evidently not easy to make. A rough idea of the probable temperature may be obtained by deductively considering the temperature gradient or, secondly, by assuming that the initial temperature of the abyssally injected basalt is not far from that of the hottest basaltic lava known in volcanoes.

The first method is only applicable on certain assumptions as to the thermal and material constitution of the basaltic substratum. It is first of all assumed that the substratum, though a true basalt for many kilometers of depth, is faintly stratified according to density differences. The chemical contrast between successive shells of the substratum may be extremely slight and yet sufficient to prevent convection-currents, even though the bottom shell of the substratum is several hundreds of degrees hotter than the uppermost shell. A rise in temperature of four hundred degrees involves an expansion of only about one per cent in volume. An underlying *couche* of basalt at 1600° C. would, therefore, if its specific gravity at 1200° C. were 2·93, not convectively displace an overlying *couche* of magma at 1200° C. and with a specific gravity of 2·90. Such faint density stratification, if assumed, goes far to explain the general stability of the earth's crust and so far is in accord with the facts of post-Archean geology. This conception also involves the possibility that the observed temperature gradient continues without important change, deep into the substratum. It is here also assumed that the gradient, 3° C. for 100 meters of descent, applies to the crust and to the upper part of the substratum at least. It must be noted, however, that the gradient may very considerably steepen in the depths, because of the fact that the thermal conductivity and diffusivity of rock both decrease in large ratio with increase of temperature. The amount of steepening of the gradient is unknown, but our ignorance on this point is unessential to the principle of the following argument, in which the normal gradient is assumed throughout.

Thirdly, it is assumed that, under normal conditions, the substratum shell immediately below the solid crust is not superheated but is at the melting-point of basalt at that depth. The accepted temperature gradient gives, at the depth of 38 kilometers, a temperature of 1140° C. Vogt has calculated that the pressure at this level raises the melting-point about 50° C. Since basalt at atmospheric pressure is just melted at about 1190° C., we may conclude that the bottom of the crust, in accordance with the assumptions, averages 38 kilometers below the present surface. If the earth is cooling down, the crust was evidently somewhat thinner during Tertiary and pre-Tertiary batholithic intrusion.

If, now, a broad geosynclinal prism of sediments, 10,000 meters thick in the middle, is laid down on the site of a future mountain-range, the isogeotherms must rise. The uppermost layer of the substratum, where most deeply buried, will thus tend to assume a temperature of nearly 300° C. above normal. If the sedimentary prism be folded and overthrust as in the usual large-scale orogenic disturbance, the substratum below the mountain-range may be still more effectively blanketed, with a further rise of the isogeotherms. Quickened erosion may, however, largely offset this thickening by the mountain-building process, and it would be unsafe to postulate a total rise of temperature of more than 300° C. in the substratum of the area. Part of this superheat is lost by conduction into the crust, the lower basic part of which may be thus melted. An unknown but possibly considerable fraction of the total superheat may remain in the original substratum, and this amount of superheat would characterize the basalt when rapidly injected into the crust.

In the partial release of pressure in the act of injection we have another, but probably less important, source of superheat—averaging some fraction of the 50° C. by which the melting-point is raised at the bottom of the 38-kilometer crust. A third source of superheat is found in the conversion into heat of the mechanical energy necessary for injecting a viscous melt into an opening cavity.

These three sources of superheat would alone furnish enough thermal energy to raise the injected basaltic magma from 1140° C. to some temperature short of 1500° C. or 1600° C.

The piling up of 10,000 meters of lava over a large area would have an analogous superheating effect on the substratum. This conclusion enables us to give some explanation of the fact that the lavas of Kilauea and Mauna Loa seem to be the hottest known in any volcanic vent. The vast Hawaiian lava-plateau has, apparently, been built up by the comparatively rapid effusion of basaltic flows from Pacific depths averaging 6,000 meters to heights above sea of about 4,000 meters. The unique lava-fountains of the calderas, while showing obvious evidence of considerable superfusion, are described as glowing with "white heat."* If a correct description, this implies a temperature of 1300° C. or possibly 1400° C.† Such temperature must be a minimum for the substratum which feeds the calderas, where there is continuous loss of heat in the convectively stirred lava.

Speculative argument and limited observations in nature agree, then, in fixing some such temperature as 1300° C. as a minimum for the basaltic mass injected into the crust-rock below a great mountain range.

Capacity of superheated, plutonic magma for melting and dissolving xenoliths.—Basalt must have a thermal capacity much like that of diabase at the same temperature. Barus's experiments show that the average specific heat of diabase for the interval 1300–1140° C. is ·350.‡ The heat-energy contained in the substratum, if it be superheated 160° C. above its melting-point (1140° C.), is in excess of that contained in the substratum just above its melting point by (160×·350=) 55+ gram-calories.

This surplus heat-energy is available for the fusion and assimilation of country-rock. There are good reasons for believing that the average wall-rock of granite batholiths has the composition and crystallinity of a granitoid gneiss. For purposes of calculation this will be assumed to be the fact. The average temperature of the wall-rock before an abyssal intrusion may be conservatively estimated from the normal temperature gradient to be 200° C. In order to raise the gneiss to the temperature of 1200°, where it is just molten,

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* J. D. Dana, Characteristics of Volcanoes; New York, 1891, p. 200.

† LeChatelier and Boudouard's High Temperature Measurements; New York, 1904, p. 246.

‡ C. Barus, op. cit., p. 53. For the interval 100–20° C. the mean specific heat is about ·185. There is, in fact, a steady increase in the mean value as the temperature of any silicate or silicate mixture rises. This fact goes far to explain the prolonged liquidity of assimilating magmas. Cf. J. H. L. Vogt in Christiania Videnskabs-Selskabets Skrifter, math-naturv. Klasse, 1904, No. 1, p. 40.

about 410 calories (assuming latent heat at 90 calories—a value estimated by Vogt for the silicates) per gram must be supplied from an outside source. If all the superheat of the basalt were available for melting (not dissolving) gneiss, $\frac{55}{410}$ of mass-unit of gneiss would be melted by mass-unit of the superheated basalt; or about 7·5 mass-units of the basalt would melt a mass-unit of wall-rock.

Such simple melting would, however, not occur. There are plenty of field and laboratory proofs that molten basalt, even slightly superheated, will dissolve fragments of gneiss and allied rocks. The mutual solution of two contrasted silicate mixtures takes place at a certain temperature which is lower than the melting point of either one. The simple contact of two such materials suffices to cause their mutual solution at that lower temperature.* This fundamental law of physical chemistry has been experimentally demonstrated for silicates by Vogt and by Doelter and his pupils, although the last mentioned authors have, perhaps, not sufficiently regarded the fact that it takes considerable time for the mutual solution to take place.†

Petrasch has experimentally shown that, when two parts of limburgite and one part of granite are mixed and heated, they melt together at 950° C. and the solution remains fluid down to 850° C.‡ Predazzo granite softens at 1150° C. and the limburgite at 995° C.§ In this case, there is a lowering of 200°–300° below the melting-point of granite and 45°–145° C. below that of limburgite.

It seems highly probable, thus, that gneiss-xenolith and basalt would form a solution or syntectic film which is molten at a temperature *at least* 50° C. below the fusion-point of basalt at the average depth of ten kilometers or less below the earth's surface. At those depths basalt melts at about 1100° C.; the syntectic would be molten at or below 1050° C. If the syntectic film were continuously removed during the sinking of the block or by the currents inevitably set up during stoping,

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*Cf. O. Lehmann, Wiedemann's Annalen der Physik, vol. xxiv, p. 17, 1885.

†See J. H. L. Vogt, Christiania Videnskabs-Selskabets Skrifter math.-naturv. Klasse, 1904, No. 1, p. 191; and Tscherm. Min. u. Petrogr. Mitth., xxiv, p. 473, 1906.

‡K. Petrasch, Neues Jahrb. für Min., etc., Beil. Bd. xvii, 1903, p. 508. Petrasch mixed the powders of one part of granite (softens at about 1150° C.) with two parts of hornblende-andesite (softens probably about 1050° C.) and found the mixture to become molten at 900° C., proving again an important lowering of the melting-point below that of either rock. Basic rock thus acts as a flux for granite (or gneiss) to an extent comparable with that proved by Petrasch and others for lithium chloride, calcium fluoride, ammonium chloride, sodium tungstate, etc.

§C. Doelter, Tscherm. Min. u. Petrogr. Mitth., xx, 1901, p. 210.

nearly all of the superheat of the basalt might be used in dissolving the gneiss. The total melting-heat of gneiss, if molten at 1050° C., would be about 400 calories. The heat-energy required for the solution of one gram of the gneiss which has an original temperature of 200° C. is $(400-40=)$ 360 calories. The heat-energy given off by one gram of basalt in cooling from 1300° to 1050° C. is about $(250 \times \cdot 340 =)$ 85 calories. One gram or mass-unit of gneiss would, then, be dissolved by $\left(\frac{360}{85}=\right)$ 4·3 grams or mass-units of the primary basalt, provided all the thermal energy were used for solution.

These various calculations are obviously very crude. They take no account of conduction of heat away from the batholithic mass, nor any account of possible exothermic or endothermic chemical reactions between basalt and wall-rock; nor any account of the influence of water, chlorides, etc., derived from the geosynclinal rocks which are assimilated.* These substances held in the magmatic solution tend to lower the solidification point of the syntectic. The result of the calculation would also be affected if we assume that the heavier xenoliths would sink to levels where the temperatures are above 1300° C. Finally, the result would be different if we postulate that the invaded formations, through the crushing incident to orogenic movement before the intrusion, had been heated above 200° C. Without here entering on the discussion of these further complications, we may conclude that probably from four to six volumes of the superheated primary basalt would furnish the heat-energy necessary for the solution of one volume of wall-rock.

If this rough estimate is even approximately correct, we have some idea of the actual assimilating power of plutonic magma which has been superheated a couple of hundred degrees. We also see a definite reason for the fact that post-Archean granites have never, so far as known, stoped their way to the earth's surface. The crust has been too thick, the expenditure of heat-energy in forming the syntectic magma too vast, that the process could operate to its extreme and so endanger the stability of the crust-roof above each batholith.

Objection founded on rarity of evidences of assimilation at observed wall-rocks.—One of the most commonly expressed objections to any theory of the replacement of invaded for-

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* According to the stoping hypothesis almost all of the heat conducted into the shells of country-rock successively stoped away during the magmatic period, is not lost, but is available for the abyssal assimilation of the engulfed blocks. In view of the slowness with which the mixtures of powdered silicates melt, it is probable that notable exothermic reactions do not take place. The possibility of endothermic reactions seems to be a more open question.

mations by batholithic magmas consists in emphasizing the obvious fact that the average xenolith and average wall-rock of batholiths do not show direct evidence of melting or of solution in the granitic magma. This objection has been answered by the writer in several publications* and also by Andrews in most vivid fashion.† The point has, however, been restated by several authorities without any adequate discussion of the subject. No one can deny that, when the magma is all but frozen, it is incapable of assimilating xenolith or wall-rock on any large scale. The practical question is as to the magma's efficiency during the long antecedent period of its history. It is true that bed-ridden centenarians did not build the pyramid of Cheops; it does not follow that men did not build it.

If it be assumed that the quartz of granite has crystallized at or below 800° C.,‡ it follows that complete rigidity is not established in a granite batholith until it has cooled to at least 800° C. Down to about that temperature limit (of undercooling), therefore, magmatic stoping is still possible. The lowest limit of active assimilation cannot well be much below 1000° C., while the temperature required to melt the average xenolith is about 1200° C. As the viscosity of granitic magmas increases greatly below 1200° C., diffusion and convection must become rapidly inadequate to remove syntectic films at main contacts, so that the molecular lowering of the fusion-point will be confined, within the interval 1200°–800° C., chiefly to the sunken blocks. It follows, first, that in the very long period of time occupied in the cooling of a plutonic mass from 1200° C. to 800° C., there will be little or no melting or solution of wall-rock; secondly, that many shells of roof-rock, perhaps aggregating thousands of feet in thickness, may be stoped away during that same period of time. In other words, because the shatter-period is longer than the period of active assimilation at the roof, it is an essential feature of the stoping hypothesis that neither visible xenolith nor main wall of a granite batholith should normally show a collar of assimilation. So far from being a difficulty, the fact that this is generally true is a distinct argument in favor of the stoping hypothesis.

Abyssal assimilation.—In the first paper of this series the writer stated grounds on which one must believe in the complete solution of engulfed xenoliths. One has only to imagine a block of gneiss, say ten meters in diameter, sinking through a column of superheated basalt twenty or thirty kilometers

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*This Journal, xv, p. 281, 1903; Bull. Geol. Soc. of America, xvii, p. 372, 1906.

†Records, Geol. Surv. of N. S. Wales, viii, Pt. 1, p. 126, 1905.

‡Cf. A. L. Day and E. S. Shepherd, Jour. Amer Chem. Soc., xxviii, p. 1099, 1906.

deep, to become convinced of the ultimate fate of that block. If the somewhat cooled lavas described by Lacroix,[*] von John,[†] Dannenberg,[‡] Sandberger[§] and others could dissolve rock-inclusions in the notable way described by those authors, we must credit a vast solutional efficiency to plutonic magma when it attacks similar blocks in great depth. The lava has a few hours or days in which to do its work; the abyssal magma has centuries if not a large part of a geological period!

It must be remembered that geosynclinal sediments are rocks unusually rich in water, chlorides, sulphur trioxide, etc.; all substances aiding solution in the primary magma and in the secondary (syntectic) magma itself. It is probably also owing to these fluids in large part that granitic magmas have crystallized at comparatively low temperatures.

The conception of stoping with abyssal assimilation has many more points in its favor than can be cited for pure marginal assimilation. A few of the special grounds for preferring the newer to the older hypothesis may be noted.

First, marginal assimilation is largely effective only in the earliest part of the magma's history, when it is absolutely and relatively very hot. There is thus an early time-limit fixed for the gigantic work of dissolving the thousands of cubic kilometers actually replaced in the intrusion of a large batholith.

Secondly, the assimilation, on the older view, takes place primarily on main contacts and along a relatively limited amount of surface. For example, a cube of wall-rock one kilometer in diameter can offer only about 1,000,000 square meters of surface at a time to the dissolving magma. If that same cube were shattered into cubes 10 meters on the side and then engulfed, the magma would carry on the work of solution on 600,000,000 square meters of surface.

Thirdly, the average crust-rock being allied chemically to gneiss, is more soluble in basic magma than in acid. On the stoping hypothesis, solution of the xenolith generally occurs in the lower, basic part of the magmatic chamber; on the older view, it is granitic magma which must do most of the work of solution. For even if the originally injected magma is a basalt, the products of its assimilating activity, being more acid and less dense than itself, must remain at the batholithic roof and rapidly assume the chemical composition of mean mountain-rock. It follows that the primary magma must be enormously more superheated than is required on the stoping hypothesis or than seems easy of explanation, in view of the

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[*] Les Enclaves des Roches Volcaniques, Macon, 1893.

[†] Jahrb, d. k. k. Reichsanstalt, Vienna, lii, p. 141, 1902.

[‡] Tscherm. Min. u. Petrogr. Mitth., xiv, p. 17, 1895.

[§] Sitzungsber. K. Bair. Akad. Wiss., p. 172, 1872.

difficulty of understanding how plutonic magma, which is capable of intrusion, can become superheated more than two or three hundred degrees Centigrade.

Fourthly, the stoping hypothesis has the special advantage of providing a mechanism of thorough agitation within a batholith. Strong stirring of the mass is induced by the sinking of xenoliths and by the necessary rising of the magma locally acidified by their solution. This agitation can explain the marvelous homogeneity in each large batholith. It helps greatly to explain the manifest evidences of magmatic differentiation within batholiths—splittings and segregations that cannot be due to the slow process of molecular diffusion or to mere thermal convection. The whole process of stoping and the rising of syntectic magma tends to equalize the temperatures in the batholithic chamber and thereby we can understand the even grain and rapid, nearly simultaneous crystallization of a batholith throughout its visible depth.

Fifthly, the engulfment of blocks of geosynclinal sediments enriches all parts of the batholiths with water, chlorides, etc. which so greatly aid solution ; while, on the older view, these agents are confined to the uppermost part of the chamber.

Sixthly, as already noted, the cleansing of syntectic films from contact of solid and liquid is much the more rapid and perfect according to the stoping hypothesis, thus providing and renewing conditions for molecular lowering of the fusion-point along contacts.

In short, the newer view has the advantage of not only better explaining the facts of the field but it is incomparably more economical of the heat postulated for the work of batholithic replacement than is the theory of pure marginal assimilation. Melting and marginal assimilation of country-rock takes place in the initial, superheated condition of a basaltic injection, but must be regarded as always subordinate in replacement efficiency to stoping and abyssal assimilation.

Existence of basic stocks and batholiths.—Finally, the fact that some large bodies of plutonic rocks are basic has been advanced as an objection against the idea of stoping.* This fact early impressed itself on the present writer and led to his reviewing the geological literature to determine, if possible, the number, distribution, and age of these bodies. It was found that most of those which have undoubtedly batholithic development on a large scale are of pre-Cambrian age and are chiefly anorthosite intrusions. In this Journal, vol. xx, 1905, p. 216, the guarded suggestion was made that the anorthosites of Canada and the Adirondack Mountains are so basic because of the absorption of crystalline limestones. On more

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* W. Cross in Science, xxv, p. 620, 1907.

mature consideration this suggestion seems inadequate and a more general explanation must be sought.

Adams describes the great anorthosite mass of Morin, Quebec, as genetically associated with an adjacent gabbro body of batholithic size.* The one is either a differentiate from the other or both are expressions of a common basic magma. The latter seems the more probable relation. In fact, both batholiths appear to represent the crystallized products of a magma allied to, if not identical with, the primary basaltic magma which has been the source of the heat in post-Archean batholithic intrusions.

The conditions of intrusion for these "upper Laurentian" masses seem to have differed from those typically represented in the post-Cambrian batholiths. The latter have been developed under heavy geosynclinal covers which have entailed considerable superheat in the basaltic substratum. It is not impossible that the "upper Laurentian" basic magmas, already cooled nearly to the solidification-point, were injected into the then thinner crust, or warped up with it, during crustal disturbance. Lacking superheat these magmas lacked stoping and assimilating power and, consequently, did not become acidified.

In favor of the conception that these magmas were near the solidification point at the time of their intrusion, is the fact that the anorthosites often show primary banding and are most extraordinarily granulated, as if by dynamic force which acted on the congealing mass near the close of the intrusion-period. Concerning the granulation Adams writes: "There are no lines of shearing with accompanying chemical changes, but a breaking up of the constituents throughout the whole mass, though in some places this has progressed much further than in others, unaccompanied by any alteration of augite or hypersthene to hornblende, or of plagioclase to saussurite; these minerals though prone to such alteration under pressure remaining quite unaltered, suffering merely a granulation with the arrangement of the granulated material in parallel strings. This process can be observed in all its stages, and there is reason to believe that it has been brought about by pressure acting on rocks when they were deeply buried and very hot. The anorthosite areas, of which there are about a dozen of great extent with many of smaller size, are distributed along the south and southeastern edge of the main Archean protaxis from Labrador to Lake Champlain, occupying in this way a position similar to that of volcanoes along the edge of our present continent." †

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* Canadian Record of Science, 1894–5.

† F. D. Adams, Jour. of Geol., i, p. 334, 1893.

Cushing and Kemp have published somewhat detailed accounts of the anorthosite forming a post-Grenville and pre-Cambrian batholith and its satellitic stocks in New York state.* The batholith covers about 3000 square kilometers in area. Cushing's petrographical descriptions show many points of agreement with Adams's description of the yet vaster Canadian batholiths. The anorthosite generally crystallized with exceptionally coarse grain and a porphyritic structure. Intense granulation is here again the rule, and from Cushing's published data it seems probable that the granulation followed hard after the act of intrusion. The characteristics and field-relations of the anorthosite are such as to suggest that they have resulted from abyssal injections of magma which was not superheated. A limited amount of stoping is possible in such a magma but extensive assimilation of country-rock is not possible for that magma.

Kemp has suggested that the New York anorthosite has, through fractional crystallization and the settlement of the basic minerals of early generation, been derived from a normal gabbro. † This idea may possibly explain the existence of the more pyroxenic contact-phase regularly occurring in the batholith. The contact rock is either gabbro or anorthosite-gabbro. It may represent the original magma but little affected by the settlement of the crystals of iron-ore, pyroxene and olivine. In the more slowly cooled interior of the mass their settlement could take place on a large scale.‡ In the Canadian batholiths this differentiation by fractional crystallization may have occurred just before the huge masses were injected into the crust.

The problem of the anorthosites is clearly as yet one for speculation rather than one capable of final solution. It seems proper to believe, however, that, since all or nearly all of the known anorthosite and gabbroid batholiths are of pre-Cambrian age, they owe their origin to special pre-Cambrian conditions. The stoping hypothesis as a whole expressly relates only to conditions which have characterized orogenic belts in post-Archean time.

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* H. P. Cushing, 18th Report of the State Geologist, Albany, p. 101, 1900; New York State Museum Bulletin No. 95, p. 305, 1905, and Bull. 115, p. 471, 1907. J. F. Kemp, 19th Ann. Report, U. S. Geol. Surv. pt. 3, p. 409, 1899.

† Op. cit., p. 417.

‡ Incidentally it may be remarked that the same conception might conceivably explain many internal basic contact-phases occurring in acid stocks and batholiths. This explanation is evidently opposed in principle to the prevailing view that the basic contact-shells are due either to diffusion of basic molecules toward cooling-surfaces, or to the combined influence of fractional crystallization and convection-currents in the magma. Neither of these hypotheses seems acceptable in the case of the anorthosite-gabbro batholiths, and the writer has come to question their validity as final explanations for some other types of intrusive bodies.

The gabbros of Paleozoic or later age represent bodies either too small or of too low temperature to carry on extensive stoping before their magmas became rigid. Diorite stocks and batholiths, according to the hypothesis, represent undifferentiated or but partially differentiated syntectic magma—of composition intermediate between rhyolite or granite and basalt. The average chemical analyses of the world's basalt, granite and diorite have been calculated by the writer from Osann's compilation.* It has been found that the diorite analysis is, oxide for oxide, almost the exact mean between the other two analyses.

These various considerations incline the writer to the view that the existence of a few large basic intrusions, cutting acid rocks, is not necessarily a fact fatal to the stoping hypothesis. Each of the cases needs special study, for they may shed much light on the difficult plutonic problem.

Differentiation of the syntectic magma.—In order to trace further the history of the engulfed xenoliths several principal conditions must be recognized. If the invading magma is superheated, so as to have the temperature of 1300° C., a block of heavy gneiss (sp. gr. at 20° C., 2·85) will speedily be heated to and above its own melting-point. While some of it is dissolved, much of it is converted into a molten globule of essentially pure gneiss. From Table II we see that the specific gravity of the globule would be about 2·40, while that of the surrounding primary magma would average about 2·72. This difference of density means that the globule must rise through the primary magma with a speed even greater than that with which the solid rock (specific gravity about 2·75) formerly sank.† As it rises the globule would wholly or partly mix with the primary magma. If wholly mixed the primary magma rapidly becomes a syntectic magma, approaching a diorite in composition. The molecular, syntectic film which is formed by solution along the surfaces of the block must, theoretically, contain equal parts of primary magma and xenolith material. If the former be basalt and the latter a granitoid gneiss, the film must have a dioritic composition. All three kinds of secondary magma—molten globules of gneiss, globule-material dissolved in primary magma as the globule rises, and the material formed in the molecular, syntectic film—must be considerably less dense than the primary basalt and rise toward the top of the batholith chamber. A net result of abyssal assimilation is a compound, secondary magma either dioritic or more acid than diorite.

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* Beiträge zur Chemischen Petrographie, II Teil; Stuttgart, 1905.

† The same reasoning applies to xenoliths of normal gneiss immersed in acidified gabbro or diorite magma.

This reasoning is deductive but it can in some measure be checked by actual observations. Lacroix describes blocks of gneiss up to a cubic meter in size, which have been immersed in molten basalt. By the heat of the lava the blocks have been "entirely transformed" into porous glass.* Von John has described other examples of the same transformation.† The present writer has correlated a considerable number of instances where the gravitative stratification has certainly been produced in thick intrusive sheets.‡

A number of observers have come to the conclusion that the very act of the assimilation of acid material by basalt predisposes the magma to magmatic splitting. The fullest statement of this view is given by Loewinson-Lessing, in his remarkable "Studien über die Eruptivgesteine."§ There appears to be, as it were, a steady "antagonism" between the ferromagnesian and acid-alkaline elements in magmas. This primordial tendency toward immiscibility may well explain the dominant acidity and alkalinity of the pre-Cambrian terranes in every continent. From the earliest times the granito-rhyolite magma has tended to separate from the basaltic wherever the viscosity has been sufficiently low for such splitting. For similar reasons it appears that the syntectic magma of post-Archean batholiths only reaches a stable condition when it assumes the ancient relation. In the average case the fluidity has been high enough for the splitting. In some cases, however, it was so low that the undifferentiated syntectic has crystallized as diorite and allied rocks.

When the syntectic has differentiated, the process must be primarily controlled by density, so that the acid, generally granitic, product rises to the top of the chamber. There it may become locally further differentiated through fractional crystallization or other relatively subordinate process.

Without discussing the causes of differentiation in more detail, it suffices to point out, in summary, that magmatic stoping involves the placing of gravity at the head of the list of forces which produce the actual diversity among igneous rocks. In this the stoping hypothesis is believed to match the facts observed in experimental, industrial and geological studies of silicate melts.

Origin of granite; the petrogenic cycle.—The stoping hypothesis involves a more or less definite corollary relating

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* Les Enclaves des Roches Volcaniques, p. 563-5; Macon, 1892.

† Op. cit., p. 141.

‡ This Journal, xx, p. 185, 1905; also Festchrift zum siebzigsten Geburtstage von H. Rosenbusch, p. 203, Stuttgart, 1906.

§ Comptes Rendus, Congrès géol. internat, VII^e session, St. Petersburg, p. 375, 1899.

to the genesis of granite as the staple visible material of post-Archean batholiths. Erosion has nowhere penetrated more than a few thousand meters in any of these batholiths. Considering the scale of operations, it follows that practically all post-Archean batholithic rock is of secondary origin. The field-relations show that the granite often replaces much geosynclinal sediment. Thick as many geosynclinal prisms are, however, it seems clear that another large, perhaps the larger, part of the replaced rock may be pre-Cambrian crystalline materials (averaging granitoid gneiss in chemical composition) which underlie geosynclinal areas, as they apparently underlie all the continental areas. The similarity of granites throughout the world may, indeed, be explained by the uniformity of the earth's primordial, acid shell and by the relative uniformity in average chemical composition of the greater geosynclinal prisms. Where sediments only are assimilated, the secondary granite may be of abnormal composition; this is the case with the granite of the Moyie Sill.*

The longer an abyssally injected and assimilating body holds its fluidity, the more perfect should be the gravitative differentiation. During this active stage lateral fissures or laccolithic spaces may be filled with offshoots of the slowly changing magma. In general these satellitic injections should succeed each other in the order of increasing acidity. In a fully represented petrogenic cycle at a batholithic area, then, the oldest intrusion should be a rock of gabbroid (basaltic) composition and the youngest an acid granite (chemically a rhyolite or quartz porphyry). Between these two an indefinite number of intermediate rock-types varying according to their degree and kind of differentiation from the syntectic—itself continuously varying in composition—might be represented in dikes or other satellitic forms. This further deduction from our hypothesis seems to be fairly matched by the observed order of igneous intrusions about the world's batholiths.†

Again, successive batholithic intrusions in the same area should show the same law of increasing acidity with decreasing age. If, for example, a crystallized granodiorite batholith be itself attacked by a later abyssal intrusive and in large part stoped away and remelted, the secondary magma collecting at the roof of the later batholith should be more acid than granodiorite. This would be expected because the mere act of remelting entails further gravitative differentiation. Each time that a silicate mass passes through the optimum temperature for magmatic splitting—probably an interval of one or

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* This Journal, xx, p. 196, 1905.

† See first intrusion paper, p. 292.

two hundred degrees above its melting point*—the separation of its acid-alkaline and ferromagnesian elements by gravity is further perfected. Morozewicz has given a telling experimental demonstration of the process. He melted two pounds of granite and left the superheated melt in a hot part of an active glass-furnace for five days. It was then cooled to a glass. At the end of the time he found that the lower part of the melt carried 59·20 per cent of silica, the upper part 73·65 per cent; the original granite showed 68·9 per cent.† An actual case of repeated differentiation of the kind seems to be represented in the Okanagan Mountain range, where, one after another, the Osoyoos-Remmel, Similkameen and Cathedral batholiths have been intruded, and clearly in the order of decreasing specific gravity of the rocks.‡

It is, however, to be expected, on the stoping hypothesis, that the primary basaltic magma may close an entire petrogenic cycle, since the latest phase of a batholith, after crystallizing, may be fissured and injected with a small volume of the substratum. The common occurrence of diabase or prophyrite dikes in granite may be thus explained.

Origin of magmatic water and gases.—Finally, the stoping hypothesis implies that, since post-Archean batholiths have generally replaced large volumes of sediments, the volatile matter which is normally trapped within a geosynclinal prism should form an important part of the secondary magma.

An approximate idea of the amount of volatile matter in the average argillite§, sandstone and limestone of the world is readily obtained. For this purpose we may use Clarke's composite analyses of 843 limestones, 624 sandstones, 27 Mesozoic and Cenozoic shales and of 51 Paleozoic shales, together with 38 analyses of various argillites from different parts of the United States.‖ From these analyses the writer has determined, for the argillites, the average amount of water below 110° C. (H_2O-), water above 110° C. (H_2O+), carbon dioxide, carbon (and carbonaceous matter), and sulphur (in SO_3). These averages represent, respectively, 116, 116, 106, 78 and 78 typical specimens of argillite from as many localities. The averages for sandstone and limestone have been taken directly from Clarke's work and all three sets are noted in the following table:

An inspection of the table makes it clear that the total of the "combined water", carbon dioxide, carbon and carbonaceous matter, sulphur and chlorine in the stratified rocks

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* F. Loewinson-Lessing, op. cit., p. 380.

† Op. cit., p. 232. Cf. C. Doelter, Petrogenesis, Braunschweig, p. 79, 1906.

‡ Bull. Geol. Soc. America, xvii, p. 329, 1906.

§ The term "argillite" here includes both shales and slates.

‖ F. W. Clarke, Bull. No. 228, U. S. Geol. Surv., p. 20 ff., 1904.

TABLE IV.

	843 limestones	624 sandstones	116 argillites
H_2O-	·26%	·29%	1·25%
H_2O+	·73*	1·41	3·71
CO_2	38·03	2·64	2·45
C (including carbonaceous matter)	?	?	·81
S	·11	·03	·25
Cl	·01	trace	trace
Total	39·14	4·37	8·47

exposed in any geosynclinal prism must represent at least six per cent of the whole mass. It is highly probable that this minimum amount of volatile matter has similarly characterized such a series ever since the period in which the series was deposited.

No petrographer needs to be reminded that none of the commoner types of igneous rock contains anything like six per cent of original volatile matter. Nevertheless it is instructive to survey the facts actually visible in quantitative analyses of the igneous rocks. Water is the only volatile substance determined in igneous-rock analyses often enough to afford nearly reliable world-averages. From Osann's compilation the writer has deduced the average of H_2O- and H_2O+ for each of the following groups: 48 granites, 47 diorites, 12 gabbros, 24 basalts, 5 augite andesites and 11 rhyolites (Table V).

TABLE V.

	H_2O-	H_2O+
Granite	·17%	·64%
Diorite	·19	1·20
Gabbro	·26	1·35
Basalt	·73	1·03
Augite-andesite	·40	1·48
Rhyolite	·30	1·23

Clarke's averages for the volatile substances occurring in igneous rocks which have been analyzed according to approved methods are:

H_2O-	·40%
H_2O+	1·46
CO_2	·52
S	·11
Cl	·07
F	·02

Much of the combined water, probably all of the hygroscopic water, and most of the carbon dioxide of these analyzed igneous rocks are due to alteration or to absorption at the earth's surface. Allowing for that fact, it seems probable that none of the more widely distributed igneous rocks carries much more

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* Includes organic matter.

than one per cent of its own weight in volatile matter directly derived from the earth's interior.

It follows that an enormous amount of water, carbon dioxide and carbon and sulphur compounds may be given off each time that geosynclinal sediments have been assimilated by molten and then crystallized magma. From each cubic kilometer of assimilated sediments about six per cent by weight of liquids and gases must be dissolved in the syntectic magma and, as crystallization proceeds, a large part of this fluid must be expelled.

In less important degree we may expect that the remelting or solution of an igneous rock by an intrusive magma should cause the evolution of some of the fluid matter which had been, as it were, frozen into the solid rock. Lincoln has aptly called such fluids "repressed emanations."* Gautier's and Brun's experiments show that many and probably all igneous rocks give off gases on being highly heated.† Reheating after cooling causes the renewed emanation of gases. Volatile matter trapped in crystallized secondary granite may thus be driven off, if that granite be dissolved in a younger molten magma with subsequent crystallization of the syntectic.

The stoping hypothesis in its broadest statement demands, therefore, that post-Archean, batholithic granites, syenites and diorites should be accompanied by special evidences of fluid emanations.

These fluids were deposited and buried in the strata. They have been resurrected in their activity. They have "risen again", both literally and figuratively; they may be called "resurgent" emanations. The "repressed" emanations of secondary igneous rocks may similarly be liberated by the distilling action of younger magma; as these fluids become revivified in their geological activities they may be regarded as forming a second kind of "resurgent" emanations. All "resurgent" emanations are of secondary origin and, therefore, stand in contrast to "juvenile" emanations, namely, those which, for the first time, have issued from the earth's interior and become geologically active on or near the surface. Magmatic emanations are, apparently, divisible into two great classes, both of which should be recognized in complete discussions of ore-deposits.

That the stoping hypothesis stands this further test seems to the writer entirely clear. The prevalence of quartz veins and pegmatites in the walls and roofs of actual granitic, syenitic, and dioritic stocks and batholiths, and the intensity of the contact-metamorphism produced by the intrusions of, and especially the emanations from, these rocks are facts as famil-

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* F. C. Lincoln, Economic Geology, ii, p. 268, 1907.

† A. Brun, Archives des Sciences Phys. et nat. Geneva, May and June, 1905 and November, 1906; A. Gautier, Annales des Mines (6), ix, p. 316, 1906, and Econ. Geol., i, p. 688, 1906.

iar as the comparative rarity of quartz-veins and pegmatites about gabbroid masses and the comparative feebleness of the contact-metamorphism produced by gabbros. The abundant water found in obsidian and rhyolite is, in this view, largely or wholly of secondary origin. Volcanic gases may similarly be largely "resurgent" rather than "juvenile." In no case, however, would one class of emanations be represented to the exclusion of the other. For post-Archean granites the emanations are dominantly "resurgent"; for gabbros the emanations are largely or dominantly "juvenile."

Conclusion.—The first two papers of this series were written in the light of experimental results bearing on the methods of igneous intrusion. Since 1903 a number of additional leading experiments according to refined methods have been carried out by Doelter and his colleagues, by the Geophysical Laboratory staff at Washington, by Brun, Gautier, Hall, Douglas, Ladenburg and others. These later investigations, like those of Deville, Bischof, A. Becker, Lehmann, Fouqué, Michel Lévy, Cossa, Thoulet, Barus, Oetling, Hofman, Tammann, Morozewicz, Forbes, Joly, Mallet, Reade, Cusack, Weber, Åkerman, Vogt, Bartoli, Jamin, Lagorio, and others, seem to show that the physical conditions and processes involved in the stoping hypothesis have been in the main correctly stated.

It is obvious that further laboratory study of rocks on the physico-chemical side is highly desirable, but the accordance of independent experimental results now on record appears to have demonstrated: first, the enormous efficiency of thermal expansion in causing shattering stresses in solid rock; secondly, the fact that the average xenolith must sink in molten granite, syenite, diorite and acid gabbro when these magmas are under ordinary plutonic conditions; thirdly, that the sunken xenoliths must melt or become dissolved in the depths of plutonic magma, forming syntectic magma; and fourthly, that, if the primary magma is basic, the average syntectic must rise through it and thus collect at the top of the magmatic chamber.

The attempt has been made, in using the experimental results of Barus, Roberts-Austen and Rücker, Weber, Bartoli, Åkerman and Vogt, to estimate the amount of average crust-rock (gneiss) which may be dissolved in one volume of superheated primary magma (basalt). The sources of superheat in plutonic magma and a rough quantitative analysis of abyssal assimilation have been discussed. The result points to an explanation of the fact that magmatic stoping has not destroyed the roofs of post-Archean batholiths. The more general problem of the stability of batholithic covers which, on any theory of magmatic intrusion, seem to be in danger of foundering in the less dense magmas, is seen to have become less serious as that problem is viewed in the light of the new estimates of magmatic density. The possibility that some of the Archean batholiths were the scenes of actual, partial foundering of the earth's crust had been noted; the suggestion is made that, in late pre-Cambrian time, it had become thick and strong enough to inhibit extensive foundering of batholithic covers.

Various objections to the hypothesis seem to fall away so soon as they are confronted by the facts of experimental investigation on melted rocks and silicate mixtures. Other objections have been met by the facts derived from the field-work of many observers. The facts of field-occurrence and field-relations are opposed to the "laccolithic theory" and to that of marginal assimilation; on the other hand, these facts all seem to be explicable on the stoping hypothesis, which, therefore, is taken by the writer to afford the best working basis for the future investigation of granitic batholiths. In this conclusion the writer is in full agreement with Andrews and Barrell, two authorities who, with the intrusion-problem expressly in mind, have carefully scrutinized actual batholiths.

The hypothesis involves several important consequences, a few of which have been considered. If magmatic stoping and abyssal assimilation have largely operated during the intrusion of post-Archean batholiths and stocks, it follows that the material of these bodies is largely or wholly of secondary origin. In each case it is a differentiate from a syntectic magma formed by the solution of primary (acid) crust-rock or of geosynclinal sediments in the (probably basic) magma of the substratum. The order of eruption in batholithic areas, with respect to the acidity of the rocks, need not be absolutely fixed, but should show a strong tendency toward the succession of eruptives becoming more acid with decreasing age. Lastly, since most post-Archean granites have replaced large volumes of sedimentary rock, the suggestion seems warranted that the water and other volatile matters regularly given off in great volume from granitic magma, are also of secondary origin. Geosynclinal sediments are normally charged with relatively abundant fluids; it seems inevitable that these should, in part at least, be given off during the solution of wall-rock or engulfed xenoliths in an invading magma.

The principal field-relation on which the foregoing discussion hangs is the "replacement" of country-rock by magma in the intrusion of stock or batholith. Slow digestion and solution on main contacts has caused the replacement to a limited degree, but the facts of nature seem to enforce belief in the more rapid and more important mechanical replacement through magmatic stoping.

Art. IV.—*Rhinocerotidæ of the Lower Miocene*; by Frederic B. Loomis.

Formerly the Lower Miocene beds of America were considered by vertebrate palæontologists to be practically barren of vertebrate fossils; but three years ago Mr. Peterson opened in them the Agate Spring quarries from which have been taken literally hundreds of skulls and disassociated skeletons, among which two species of rhinoceros of the hitherto rare genus *Diceratherium* are far the most abundant. In the "breaks" of the neighboring hills scattered remains have also been found, and it was the fortune of the Amherst '96 expedition, during the summer of 1907, to find a small pocket of rhinoceros bones some 300 yards north of the above mentioned quarries. These latter remains are remarkable in that they represent seven different rhinocerine species all buried together. Four of the species are new and as they represent some unexpected phases, they are not only described, but a broad study of the whole group in the Lower Miocene is here undertaken. While with the three new species added in this paper, thirteen species of Diceratherium are now known, the genus has never been carefully studied, partly because the early species assigned to it were never figured and were with difficulty accessible. For this paper the Yale Museum has allowed the study of the Marsh material and the figuring of his types, which were but briefly characterized. The following paragraphs will therefore consider the genus Diceratherium, as to its characteristics, distribution and the systematic relations of its species. The Acerathteria of the Lower Miocene will also be described, as the genus has not previously been found in the American strata later than the Oligocene.

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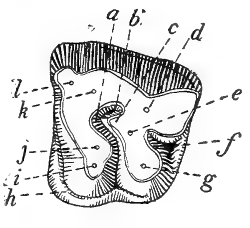

Fig. 1. *Diceratherium niobrarense P.*; second upper molar, one-half nat. size. Key to terminology: *a*, prefossette; *b*, med. fossette; *c*, crochet; *d*, metacone; *e*, metaconute; *f*, postfossette; *g*, hypocone; *h*, cingulum; *i*, protocone; *j*, protoconute; *k*, paracone; *l*, parastyle.

The genus Diceratherium was established in 1875 by Marsh for the species *D. armatum*,* its distinctive feature being the presence of a pair of horn cores on the nasal bones. While the animal was rather long-limbed and light built, as the skeletal material is mostly disassociated no attempt will here be made to discuss this part of the skeleton. The teeth vary considerably, the

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* This Journal, vol. ix, p. 242, 1875.

earlier forms from the John Day beds showing but little complication; but with the advance of time the crochet and crista develop, and increase progressively until they meet and isolate the median fossette. The premolars of any jaw grade in their characters unto the molars, but there is a tendency for the premolar to attain any feature earlier than the molar. The upper canine is wanting but that of the lower jaw is moderately developed, having a triangular cross section. The incisors are reduced to $\frac{1}{1}$, the upper one being elongated and oval in section as in Aceratherium, while the lower incisor is a mere button-like rudiment. The first lower premolar is usually wanting; so that the generic dental formula is $\frac{1}{1}\ \frac{0}{1}\ \frac{4}{3}\ \frac{3}{3}$.

It is in the John Day beds of Oregon that the first Diceratheres are found, full fledged as to the nasal horn cores; but, were only the dental series of such a form as *D. armatum* considered, the simple cross ridges and well developed cingulum, would proclaim it an Acerathere. On the other side the species *Aceratherium tridactylum* from the Protoceras beds has a pair of low roughened bosses on either nasal bone seeming to indicate incipient horns. This species was considered by Hatcher* as already a Dicerathere, but Osborn places it among the Aceratheres, where the writer would leave it, as the form still has the second upper incisor and the more dolicocephalic type of skull which characterizes the Aceratheres. However, it is, as Osborn indicates, closely related and probably ancestral to the Diceratheres, the White River Aceratheria being the stock from which the genus Diceratherium arose. The John Day species (especially *D. armatum*) are very Acerathere-like, in the strong development of the cingulum and the absence or weak development of the crochet and crista. The European species are likewise among the less specialized members of the genus; but they are differentiated by the strongly projecting protoconule fold, which has sometimes been described as an "antecrochet." It seems to the writer simply an enlargement of the protoconule region, and is characteristic of both *D. minutum* (=*crozieri*) and *D. douvillei*, and also of the American species *D. hesperium;* so that these three species make a convenient and related sub-group. The later American forms from the Lower Harrison beds all have crochet well developed, *D. niobrarense* being the simplest of them, and having an aspect very suggestive of the John Day phase. The other species have a crista, which the crochet tends to meet. On the wall of the crochet away from the median fossette are often tiny ridges which give the enamel a characteristic wavy appearance. The latest species known is *D. oregonensis*, in which the crochet and crista are broadly united.

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* Amer. Geologist, vol. xx, p. 313, 1897.

During Oligocene times the country west of the Great Lakes and either side of the Canadian line seems to have been teeming with Aceratheres, abundant in numbers and varying in characteristics. At the end of the Oligocene all but a remnant of this rich fauna disappeared, its descendants in Europe still flourishing while but a handful still held on in America, as will be shown later. Why the disappearance is unknown. Directly succeeding these Aceratheres, it now appears that the Diceratheres flourished, apparently as rich in numbers and in species. While longer limbed and somewhat shorter headed, the dentition forbids any thought that these were open country creatures. There are no nibbling teeth and the backs of the canines are worn as when branches are stripped of leaves by drawing them through the mouth. The grinders are also those of a brouser. Spreading westward and northward, these Diceratheres crossed the Berings isthmus and reached Germany and France, there to become in a short time extinct. In America they multiplied in Lower Miocene times, and in the Harrison period no less than five* species were ranging over Nebraska and Wyoming. In their turn the Diceratheres as mysteriously wane and die out, the last one known being only indicated by a single tooth from the Upper Miocene of Oregon.

Throughout the genus, the size and shape of the nasal horns vary in any species with the age and sex of the individual. Variation is also characteristic in the weight and stockiness of the skull as a whole. In all features there is that tendency to fluctuation which is found in a young and developing group, the different species representing apparently points in evolutionary lines. Some of the species can be gathered into subgroups on common features which represent common descent, but there are still many gaps to be filled before a perfect case of adaptive radiation will be illustrated. The characters which have proven most satisfactory for establishing species are, after size and contour of the skull has been considered in a general way, the pattern of the premolar and molar teeth.

In the following descriptions the Osborn nomenclature has been used, a key to which is given in fig. 1, p. 51. The figures are all one-half natural size except fig. 10. Further measurements are given in the table at the end of the descriptions of the genus Diceratherium.

Diceratherium armatum Marsh.

This Journal, vol. ix, p. 242, 1875.

The type is No. 10,003 in the Yale Museum, a complete skull somewhat crushed dorso-ventrally, from "near John Day River in Eastern Oregon."

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* Probably as many more will turn up within a few years, judging from the variation of toe bones and other of the less characteristic features.

Thus, the largest species of the Diceratheres is characterized by the simplicity of the dental pattern, the crista and the crochet being absent on the second and third molars, and only the crochet faintly indicated on the first molar. The premolars are without the crochet but have the crista incipient. Around the premolars the cingulum is well developed along the front, back and internal face of the tooth; but in the first molar it is interrupted opposite the protocone and hypocone.

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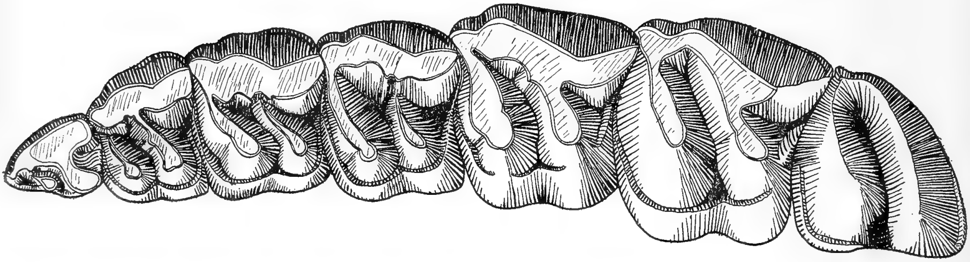

Fig. 2. *Diceratherium armatum* M.; premolars and molars of type specimen, one-half nat. size.

As noted above, in the simplicity of the dental pattern and in the development of the cingulum, *D. armatum* shows a strong affinity to such Aceratheres as *A. tridactylum* and *A. occidentale*.

Diceratherium annectens Marsh.

This Journal, vol. v, p. 4, 1873.

The type is No. 10,001 of the Yale Museum from the "John Day valley, Oregon." The type is composed of the incisor, first and third premolars, and the first and second molars, of the upper right jaw, apparently all belonging to one individual. Of these the second molar is marked "type," but the others are included in the description.

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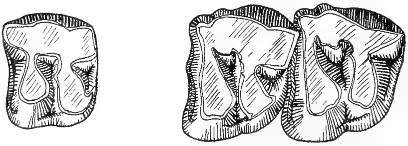

Fig. 3. *Diceratherium annectens* M.; third premolar, first and second molar of type specimen, one-half nat. size.

This small species is readily distinguished by the fact that on the molars the protoconule and the hypocone are so closely placed that on a partly worn tooth they actually join and the intervening valley between the protoloph and the metaloph is interrupted. The crochet is only incipient; and the crista, while wide, is not prominent. The cingulum is well developed in front and behind, but internally is wanting except for a trace between the protocone and hypocone.

Diceratherium nanum Marsh.

This Journal, vol. ix, p. 243, 1875.

The type is No. 10,004 in the Yale Museum from the John Day River in eastern Oregon. The specimen is the front of a skull including the upper and lower incisors, the lower canines and the first three upper and lower premolars; all however worn to the roots, so that the dental pattern is obliterated, and the only available character is size. In this it agrees closely with *D. annectens*.

4

FIG. 4. *Diceratherium nanum* M.; incisor and first three upper premolars of the type, one-half nat. size.

Diceratherium hesperium Leidy.

Proc. Acad. Nat. Sci., Phila., p. 176, 1865.

The type in this case is a lower molar from the John Day of Oregon. Later to this, Leidy assigned some further fragmentary material, in which was a third upper molar, which is so far the only distinctive specimen. The lower molar used as type is intermediate between *D. armatum* and *D. annectens*, and while it will never be certain that the assigned specimens are the same species, there seems to be a distinct species of this size, which they may well typify. The features of the third upper molar* are that the protoconule and the metacone are much swollen, and there is a small tubercle in the valley between the protocone and the hypocone.

Diceratherium pacificum Leidy.

Proc. Acad. Nat. Sci., Phila., p. 248, 1871.

This type is again fragmentary material from the John Day of Oregon. Here the first molar tooth described is a second upper molar from the right side, which indicates a well marked

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* See Rep. U. S. Geol. Surv. Terri., vol. i, pl. ii, fig. 8.

species, characterized by the presence of two moderate crochets, and two strong cristæ. The cingulum is well developed both in front and along the internal face of the tooth.

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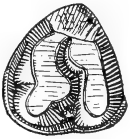

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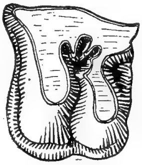

FIG. 5. *Diceratherium hesperium;* after Leidy, one-half nat. size.
FIG. 6. *Diceratherium pacificum* L.; the second upper molar, after Leidy, one-half nat. size.

The writer will be surprised if the second tooth assigned to this species by Leidy* does not prove to belong to some as yet undescribed species. The entire lack of crista and crochet would debar it from belonging to this species.

Diceratherium niobrarense Peterson.

Science, vol. xxiv, p. 281, 1906.

Type is No. 1,271 in the Carnegie Museum, a nearly perfect skull from the Lower Harrison beds of Agate Spring Quarry, Sioux Co., Nebraska.

The species is characterized by moderate size, the skull being relatively narrow and high, with a comparatively small brain case. The occipital crest is high, and joined by a strong sagittal crest formed by the union of the ridges from over the orbits. The nasal bones project considerably beyond the horn cores: the orbit is large; and the wide zygomatic arches are heavy. Of the teeth the premolars have preserved the cingulum intact along the inner face, and are without either crochet or crista. The molars are in like manner primitive, having the internal cingulum only slightly interrupted opposite the hypocone, while the crista is wanting and the crochet quite moderate in development. As noted by Peterson, the species resembles *D. armatum* of the John Day and is probably a direct derivative of that form, having advanced in the moderate development of the crochet and in the skull becoming narrower and higher. In size it is about 4/5 as large as *D. armatum*. See fig. 1 on page 51, and for further figures see Peterson.†

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* See Rep. U. S. Geol. Surv. Terri., vol. 1, pl. ii, fig. 7.
† Ann. Carnegie Museum, vol. iv, p. 46, 1906.

Diceratherium petersoni sp. nov.

Type is No. 1,583 in the Amherst College Museum, being the first and second upper molars, found in the Lower Harrison beds, 300 yards north of Agate Spring Quarry, Sioux Co., Nebraska. Named for Mr. O. A. Peterson, who has made the Lower Harrison fauna, especially the Diceratheres, famous.

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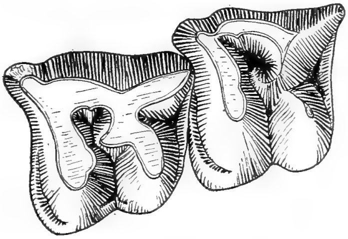

FIG. 7. *Diceratherium petersoni;* first and second molars (type specimen), one-half nat. size.

The species is the largest of those from the Lower Harrison and closely approximates *D. armatum* in size. The anterior cingulum is reduced and the internal one absent except for a trace between the protocone and the hypocone on the first molar. The crochet is strongly developed but not united to the distinct, though small, crista. In specialization this species is intermediate between *D. niobrarense* and *D. schiffi.*

While no skull was found, numerous scattered teeth were collected.

Diceratherium schiffi sp. nov.

Type is No. 1,042 in the Amherst College Museum, being an incomplete skull, including the right upper premolar and molar dentition together with the entire brain case, from the Lower Harrison beds, 300 yards north of Agate Spring Quarry, Sioux Co., Nebraska. The species is named to honor Mr. M. L. Schiff, one of the supporters of the expedition on which the type was found.

The species is the smallest and most specialized of the genus so far found. The low flat skull has an unusually wide brain case. The occipital crest is low and the ridges from over the orbits fail to unite in a sagittal crest, but remaining wide apart in both young and old individuals, cause the flat dorsal surface between the orbits to extend back to the rear of the skull. The orbit is large, and the zygomatic arch moderate both in weight and width. On the premolars the internal cingulum is incomplete. The crochet and crista are united, thus isolating the median fossette, and on the outer face of the crochet wall are tiny ridges which gave a crenulated appearance to the enamel wall when worn. On the molars the anterior cingulum is weak, the internal one wanting, and that on the posterior border is raised. While the crochet is large, it does not unite with the moderate crista. The species has affinities with *D. cooki*, but is smaller and of lighter build; has a wide flat skull in contrast to the high and narrower one of *D. cooki.* It has also the crista better developed.

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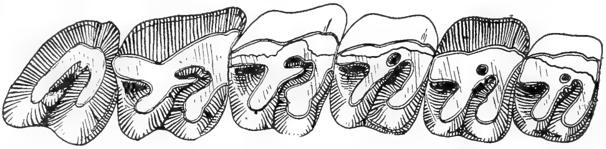

Fig. 8. *Diceratherium schiffi ;* left upper premolar and molar series of the type ; one-half nat. size.

In the experience of the Amherst part this was the commonest species, there being in the collection three incomplete skulls and several jaws.

Diceratherium cooki Peterson.

Science, vol. xxiv, p. 281, 1906.

The type of the species is a skull in the Carnegie Museum, from the Lower Harrison beds of the Agate Spring Quarry, Sioux Co., Nebraska.

The heavily built skull is relatively short and high, with a high occipital crest and a moderate sagittal crest formed by the confluence of the two ridges from over the orbits. The orbit is small, and narrow zygomatic arch of moderate weight. The nasal bones do not project in front of the horn cores, but end abruptly, giving the skull a very characteristic appearance. On the premolars, the cingulum is greatly reduced; while the strong crochet unites with the feeble crista, thus isolating the median fossette. In like manner on the molars, the cingulum is reduced to traces on the front, inner side, and rear of the teeth. The crochet is very large and the crista weak, but the two do not unite.

As noted above, this species resembles in dentition *D. schiffi*, but has a shorter and higher skull, with a sagittal ridge, where the latter has a broad flat area. The crochet is larger and the crista weaker than in *D. schiffi.*

Diceratherium aberrans sp. nov.

Type No. 1,321 in the Amherst College Museum, a single tooth, being either the first or second upper right-hand molar, from the Lower Harrison beds near Agate Spring Quarry, Sioux Co., Nebraska. While a single tooth is undesirable for a type, this is so aberrant and specialized that the writer feels bound to call attention to it.

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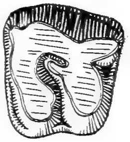

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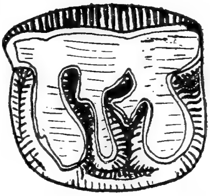

FIG. 9. *Diceratherium cooki* P.; a second upper molar, one-half nat. size.
FIG. 10. *Diceratherium aberrans;* type specimen, nat. size.

The small tooth is considerably longer than wide, which is unusual among the Diceratheres. Its cingulum appears as remnants along the front and inner faces. The striking feature, however, is the development of the crista until it almost equals in length the protoloph, having on its anterior side a strong crochet-like process. In like manner the crochet is developed to enormous size, and extends to the crista though it does not unite with it. The great development of these two usually moderate processes spreads the protoloph and metaloph wide apart, causing the considerable lengthening of the tooth.

Diceratherium minutum Cuvier = *D. Croizeti* Pomel.

See Osborn, Bull. Amer. Museum Nat. Hist., vol. xiii, p. 237, 1900.

This form from France and Germany is one of the simpler types of the genus, and occurs in the Upper Oligocene apparently equivalent to the John Day. On both molars and premolars the internal cingulum is greatly reduced, and the crochet is but little developed, while on only unworn teeth can any crista be detected. The region of the protoconule is much swollen, making a fold which is very characteristic of the European forms and has been termed an "antecrochet," though the writer cannot feel that it is the true one.

Diceratherium douvillei Osborn.

Bull. Amer. Museum Nat. Hist., vol. xiii, p. 239, 1900.

A second European species from the Lower Miocene (Burdigalian) of France. It is differentiated by Osborn by its size, the well-developed crochet, no crista, and a large "antecrochet," this being as above the swollen protoconule fold. This and the foregoing species are closely related to each other and represent the European invasion of these American Diceratheres. The two species with their swollen protoconule folds show also relationship to the little known *D. hesperium.*

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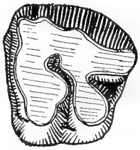

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FIG. 11. *Diceratherium minutum;* second molar, after Cuvier, one-half nat. size.
FIG. 12. *Diceratherium douvillei;* second molar, after Osborn.

Diceratherium oregonense Marsh.

This Journal, vol. v, p. 5, 1873.

The type is a broken molar tooth from the Loup Fork of Oregon. This very much worn tooth shows the continuation of the features of *D. schiffi* and *D. cooki*, the crochet having united with the crista and thus isolated the median fossette. The internal cingulum is well developed. This is the latest known Dicerathere, and in all probability the genus became extinct during early Loup Fork times.

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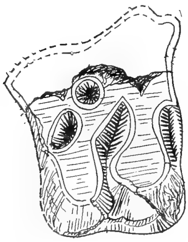

FIG. 13. *Diceratherium oregonense;* type specimen, being probably molar 2, one-half nat. size.

Beside the rich fauna of Diceratheres, two Aceratheres have been found within the past year in these Lower Harrison beds; a matter of considerable interest, as it has heretofore seemed that except for the species of Aceratherium which migrated to Asia and Europe, the genus had died out in America. It now appears, however, that a few forms maintained themselves in this country at least as late as the Lower Miocene. The two species show but slight modification from their Oligocene progenitors, as will be seen from the following descriptions and figures.

Aceratherium stigeri sp. nov.

Type is No. 1,040 in the Amherst College Museum, a skull lacking only a part of the occipital crest and the premaxillæ, from the Lower Harrison beds, 300 yards north of Agate Spring Quarry, Sioux Co., Nebraska. The specific name is given to honor Mr. W. D. Stiger, an earnest promoter of the expedition on which the type was found.

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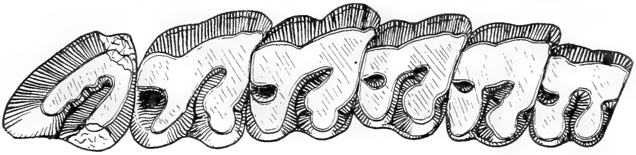

Fig. 14. *Aceratherium stigeri;* the premolar and molar series of the type specimen, one-half nat. size.

The small skull is elongated, light in build, and rather narrow. The orbit is large and the zygomatic arch light. The premolar teeth are crowded, there being neither an anterior or posterior cingulum, though one is developed along the inner face around the protocone, running out on the hypocone. Crista and crochet are wanting on these teeth of a rather old individual, except that on the fourth premolar there is a faint trace of a crista, and on the third premolar a small antecrochet is developed. On the molars the cingulum is reduced as in the premolars; and both crochet and crista are wanting. The protoconule, however, is swollen, making a considerable fold as in European Diceratheres. *A. stigeri* is closely related to *A. egrerius*, but is smaller and has the cingulum on the premolars and the crochet on the molars less developed.

Measurements.

Total length of the skull	about 345^{mm}
Width between the orbits	117^{mm}
Length of the premolar-molar series	168^{mm}
Length of second molar tooth	29^{mm}
Width of second molar tooth	37^{mm}

Aceratherium egrerius Cook.

Science, N. S., vol. xxvii, p. 256.

Type a skull and lower jaws in the private collection of Mr. Harold Cook, from the Lower Harrison beds, at Agate, Sioux Co., Nebraska.

This larger species has an elongate skull, of moderately light build, the facial portion being unusually elongated; so that the

CHART OF THE SPECIES OF DICERATHERIUM

Name	Age	Length of skull	Breadth* of skull	Height † of skull	Length & breadth of molar 2	Premolar characters	Molar characters	Remarks
D. armatum	John Day	557mm	230mm		50 × 58mm	Internal cingulum complete No crochet No crista	Internal cingulum incomplete Crochet incipient No crista	
D. annectens	John Day				28 × 36	Internal cingulum a mere trace Crochet incipient No crista	Internal cingulum a mere trace Crochet incipient Crista weak	Protoconule and hypocone very close
D. hesperium	John Day						Internal cingulum complete Crochet? No crista	Protoconule and metacone swollen
D. pacificum	John Day				33 × 40		Internal cingulum complete 2 crochets 2 cristæ	
D. niobrarense	L. Harrison	458	168	150mm	40 × 45	Internal cingulum complete No crochet No crista	Internal cingulum nearly complete Crochet moderate No crista	
D. petersoni	L. Harrison				45 × 48		Internal cingulum a mere trace Crochet strong Crista weak	

CHART OF THE SPECIES OF DICERATHERIUM—CONTINUED

Name	Age	Length of skull	Breadth* of skull	Height† of skull	Length & breadth of molar 2	Premolar characters	Molar characters	Remarks
D. schiffi	L. Harrison		132$^{\text{mm}}$	125$^{\text{mm}}$	30 × 33$^{\text{mm}}$	Internal cingulum incomplete Crochet united to crista Minor ridges on crochet	Internal cingulum lacking Crochet large Crista moderate	Skull flat where sagittal ridge usually occurs
D. cooki	L. Harrison	348$^{\text{mm}}$	143	144	31 × 34	Internal cingulum lacking Crochet united to crista	Internal cingulum lacking Crochet very large Crista weak	Skull high with sagittal ridge
D. aberrans	L. Harrison				24 × 20		Internal cingulum a trace Crochet enormous Crista as long as the protoloph	
D. minutum	Upper Oligocene				32 × 36	Internal cingulum a mere trace Crochet incipient Crista wanting	Internal cingulum a mere trace Crochet incipient Crista wanting	Protoconule much swollen
D. douvillei	L. Miocene				33 × 39	Internal cingulum complete Crochet double Crista wanting	Internal cingulum incomplete Crochet strong No crista	
D. oregonense	Loup Fork				40 × 55 ?		Internal cingulum complete ? Crochet united No crista	

* Breadth is measured between the orbits.

† Height is measured from under the foramen magnum to the top of the crista.

teeth are not so crowded as in the preceding species. On the premolars the cingulum extends around the front, inner, and rear faces. These premolars are very simple, showing no trace of a crista or crochet. The cingulum on the molars is interrupted on the inner face opposite both the protocone and hypocone. A crochet is moderately developed, especially on the second and third molars.

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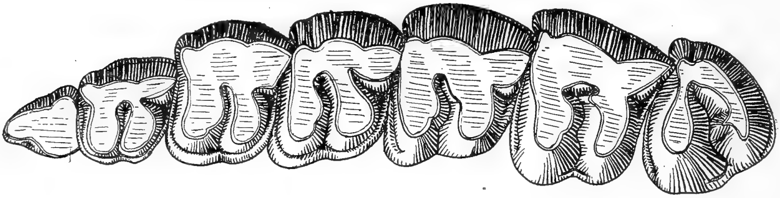

FIG. 15. *Aceratherium egrerius* C.; the premolar and molar series, one-half nat. size.

This and the preceding species show much resemblance to *A. occidentale* of the Oligocene.

Measurements.

Total length of the premolar-molar series	204^{mm}
Length of second molar	33^{mm}
Width of second molar	46^{mm}

Amherst College, Amherst, Mass.

Art. V.—*Descriptions of Tertiary Plants;* by T. D. A. Cockerell.

1. *A Frog's-bit from Florissant, Colorado.*

Limnobium obliteratum sp. nov. Figure 1*a*.

Blade of leaf nearly circular, with a reniform base; obscurely about 10-nerved, these nerves simple, and exactly as in the living *L. spongia*. Length from insertion of petiole to apex about 31^{mm}, from apex of basal lobes to apex 35; breadth 36. Margin perfectly entire, somewhat thickened. The apex is broadly rounded, with no tendency to pointing, such as is seen in the living *L. spongia*.

This is the first fossil species of this group from America; but a similar plant occurs in the Miocene of Europe, and has been named by Heer *Hydrocharis orbiculata;* "distinguished by its circular leaves, which no doubt floated on the surface of the water like the leaves of water-lilies."

Hab.—Florissant, in the Miocene shales, Station 14 (*W. P. Cockerell*, 1907). Peabody Museum, Yale, Cat. No. 1001.

2.—*Two Maples from Florissant.*

Acer perditum sp. nov. Figure 1*b*.

Leaf with the blade deeply trilobed, the sinuses extending about half way to the base; the lobes broad, pointed, the middle one broadest about 9^{mm} from its base, thence slightly contracted basally; prominent nervures three, but also a smaller one on each side; margin obscurely and rather remotely dentate. As preserved, the blade is yellowish, while the petiole and principal nerves are dark brown. Length of blade, about 44^{mm}, breadth about 34; breadth of middle lobe in middle, 12^{mm}, at base, 10^{mm}; length of middle lobe about $24\frac{1}{2}^{mm}$; of lateral lobes 20 or less. There is some resemblance to such fossil species as *Aralia notata* Ward, but the venation is very different, and agrees with that of *Acer*. *Acer narbonnense* Saporta, from the Oligocene, is a somewhat similar leaf, differing however in its margin, and in the much less broadened base. The Chinese *A. wilsoni* Rehder is similar in general form, but its lobes are far more attenuate, its margins are almost completely entire, and the extra basal (external) veins are absent. There is also resemblance to *A. saccharum rugelii* (Wesm.) Rehd., which, according to Sargent, is a leaf-form sometimes appearing on the upper branches of trees which have on their lower branches the leaves of typical *A. saccharum*. In the southern states, however, the *rugelii* form is normal, and frequently the only one present; so it may perhaps be an open question whether the appearance of *rugelii* leaves on true *saccharum* is due to reversion or to hybridization. In the position of the lobes, the fossil resembles *A. pennsylvanicum* L.

Hab.—Florissant, in the Miocene shales. Station 14 (*S. A. Rohwer*, 1907). Peabody Museum, Yale, Cat. No. 1002.

Acer florigerum, sp. nov. Figure 1*c*.

Flower; pistillate, apetalous, tetramerous. Styles two, separate to the base, long, exserted, straight or very slightly curved, about 4mm long. No sign of any stamens. Sepals four, lanceolate, pointed, only about the basal two-fifths united.

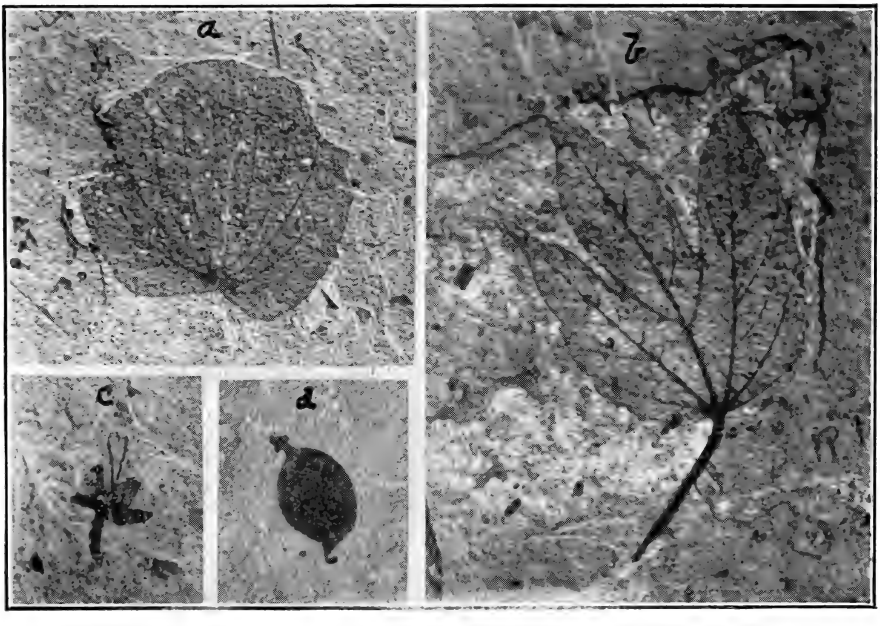

FIG. 1. (*a*) *Limnobium obliteratum*; (*b*) *Acer perditum*; (*c*) *Acer florigerum*, × 2; (*d*) *Phaca wilmattæ*.

In the form of the styles, this resembles *A. nigrum* Mx., but the calyx segments are nearly as in *A. drummondii* in form. Only four calyx segments or sepals are preserved, and there were apparently no more. The diœcious tetramerous flowers indicate affinity with such species as *A. tetramerum* Pax, *A. betulifolium* Maxim., and *A. barbinerve* Maxim.

Hab.—Florissant; Miocene shales (*W. P. Cockerell*, 1907). It was found at Station 14. I think this flower may safely be assigned to *Acer*. As it presents some interesting characters, and cannot be assigned with any degree of assurance to any particular species known by leaves or fruits, I give it a separate name. Peabody Museum, Yale, Cat. No. 1003.

3. *A Vetch Pod.*

Phaca wilmattæ sp. nov. Figure 1*d*.

Pod strongly inflated, broad-ovate in outline, 13^{mm} long and 10 broad, apparently thick, as preserved dark red-brown, tipped with a thick strongly curved style about $3\frac{1}{2}^{mm}$ long, and with a short thick stipe about 2^{mm} long, its union with the base of the pod perfectly abrupt. Calyx very small. In the form of the pod, this is more like *P. longifolia* (Pursh) Nutt., but the pod being stalked, it is so far related to *P. americana* (Hook) Rydberg.

Hab.—Florissant, Miocene shales, Station 14 (*Wilmatte P. Cockerell*). I am indebted to Miss Alice Eastwood for calling my attention to the affinities of this fossil.

Peabody Museum, Yale, Cat. No. 1004.

4. *Miocene species of Hydrangea.*

In 1885 a supposed species of *Marsilea*, found in the Upper Miocene beds of the John Day Basin, Oregon, was published by Ward. Lesquereux, in 1888, observing that the plant was certainly not a *Marsilea*, but represented a calyx of some sort, referred it to *Porana*. In 1902, however (Bull. 204, U. S. Geol. Surv., p. 60), Knowlton, following a suggestion from Pollard, referred it to *Hydrangea*; and this appears to be certainly correct.

Hydrangea has been reported to occur, with several species, in the European Tertiaries; but some of the species, at least, are doubtfully of this genus.

In addition to *H. bendirei* (Ward) Knowlton from Oregon, two species have been found in the Miocene shales of Florissant. One of these, *H. subincerta*, I have published in Bull. Amer. Mus. Nat. Hist., 1908, p. 92; the other, more recently found, is described herewith.

Hydrangea florissantia sp. nov.

Sterile flower large, the larger diameter about 21^{mm}; sepals nearly round, the larger about 10^{mm} long, the smaller about 9 (one of the smaller missing in the type); color as preserved light brown, the centre of the flower dark; venation distinct, except peripherally, nearly as in *H. bendirei*.

Evidently close to *H. bendirei*, but much smaller, more equilateral and with the shorter sepals less truncate. Very different from *H. subincerta* by the larger size and shape of the sepals.

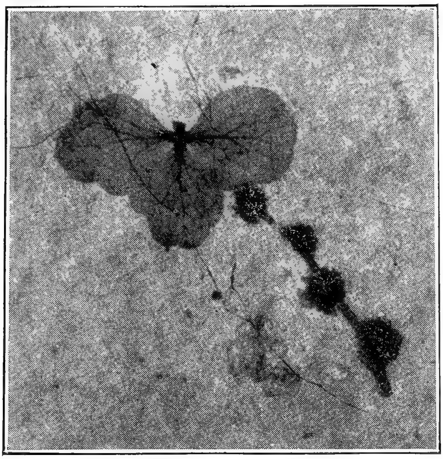

FIG. 2. *Hydrangea florissantia.*

Florissant, Miocene, Station 14 (*T. D. A. Cockerell*, 1907). Type in Yale University Museum. On the same piece of shale touching the *Hydrangea* (as shown in the figure) is what I take to be part of the male inflorescence of a *Castanea*—presumably that of *C. dolichophylla* Ckll., which is represented by leaves at Station 14.

ART. VI.—*Descriptions of Tertiary Insects;* by T. D. A. COCKERELL.

PART IV. [Continued from p. 312.]

(9) *Dragonflies from Florissant, Colorado.*

Melanagrion nigerrimum sp. nov.

WINGS hyaline basally, to about three cells beyond the quadrangle; beyond that black to apex (owing to the partial destruction of the membrane, the black is patchy and irregular; the apical field was perhaps dark brown rather than pure black); first row of costal cells broad, as in *Lithagrion;* at the tenth cell before stigma the costal cell is half size of subcostal, the latter being twice as deep; apex of quadrangle to tip of wing about $24\frac{1}{2}^{\mathrm{mm}}$ ($26\frac{3}{4}$ in *M. umbratum*), but the ten costal cells before stigma measure together about $7\frac{1}{2}^{\mathrm{mm}}$ (six in *M. umbratum*). Stigma large, about $3\frac{1}{2}^{\mathrm{mm}}$ long, bounding five cells below; costa obtusely bent at stigma, the margin beyond rapidly descending to apex; eight poststigmatal sectors; vein Cu_{2a} a little before medioanal link; base of wing agreeing in general with *M. umbratum.*

Florissant: one specimen, with reverse; Station 14 (*W. P. Cockerell*, 1907). Holotype in Peabody Museum, Yale.

Lithagrion hyalinum Scudder. Figure 1.

A specimen was obtained by Mr. S. N. Rohwer at Station 17, on a slab with *Typha lesquereuxi* Ckll.,* showing some characters heretofore obscure. There are certainly only two antenodal sectors. The stigma is swollen, and bounds $3\frac{1}{2}$ cells below. The total length of the wing is 28^{mm}; from nodus to stigma $14\frac{2}{3}^{\mathrm{mm}}$; nodus to base 9^{mm}; breadth of wing in middle 7^{mm}. These dimensions are uniformly less than in Scudder's type, but that was probably an upper wing, while ours is apparently a lower; there may also be a difference of sex. (In *Enallagma civile*, male, I find anterior wing $19\frac{2}{3}^{\mathrm{mm}}$, posterior $18\frac{1}{2}$). There are 17 sectors on costa between nodus and stigma (16 in type *L. hyalinum*), and 14 in the same distance in the subcostal series; the costal cells beyond the stigma are doubled, which is not at all the case in *Melanagrion nigerrimum* (in *M. umbratum* there is a slight tendency to doubling). There are three simple cells between M_1 and M_2 before the doubling begins.

These new materials make the genus *Melanagrion* appear less distinct than when it was proposed, *M. nigerrimum* being in some respects intermediate between *Melanagrion* and *Lith-*

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* On the other side of the slab is *Planorbis florissantensis* Ckll. (Peabody Museum, Yale).

agrion. Characteristic of both is the position of vein M_3, originating a long way before the level of the nodus, though not half-way to the arculus;—a condition found to-day in *Megaloprepus*, one of the Anormostigmatini. The question was raised, whether *Lithagrion* and *Melanagrion* could represent the stem which gave rise to the Anormostigmatini; but altogether against this is the position of the long sector between veins M_1 and M_2. Mr. E. B. Williamson writes that he regards the latter character as of considerable significance, and for this and other reasons would support Scudder's reference of the insects to the *Podagrion* series. He adds, with reference to *M. umbratum*: "it is not specialized by reduction, and the nodus is retracted as in *Paraphlebia* (but not so much as in Anormostigmatini), with which compare the more specialized *Argiolestes* and *Nesolestes*, for example."

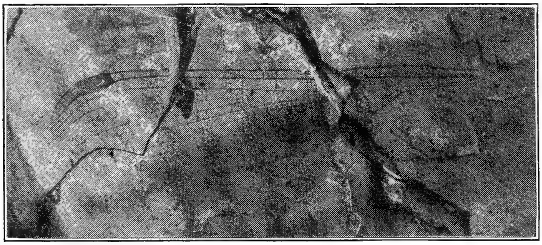

FIG. 1. *Lithagrion hyalinum.*

The following table separates the three Florissant species:

Wings hyaline; stigma bounding 3½–3¾ cells below. *Lithagrion hyalinum* Scudd.
Wings strongly infuscated; stigma bounding 5 cells below. . . . 1.
1. Apex of wings hyaline; costal cells narrow. *Melanagrion umbratum* (Scudd.).
Apex of wings dark; costal cells broad. *Melanagrion nigerrimum* Ckll.

Enallagma florissantella sp. nov. Figure 2.

Wing hyaline, about 23^{mm} long (base gone); nodus to stigma $12\frac{1}{2}^{mm}$; nervures and stigma dark sepia brown; subnodus oblique; subquadrangle not crossed; 14 costal sectors between nodus and stigma; stigma bounding one cell below; costal cells beyond stigma large; only one double cell in the series between M_1 and the sector M_{1a}, this immediately below stigma, separated therefrom by a single cell; three cells between quadrangle and level of nodus, the third very long, and represented by two cells in the series immediately below;

upper side of quadrangle not or barely longer than inner side; six cells on lower margin before Cu_2 begins to zigzag, and ten cells in the zigzag portion, making 16 cells in all from subquadrangle and end of Cu_2; three cells between M_1 and M_2 before the doubling begins; costa before nodus scarcely at all arched.

Florissant: one specimen; Station 14 (*T. D. A. Cockerell*). A poorly preserved leaf of *Ficus arenaceæformis* Ckll. is on the same slab. The figured specimen is in Peabody Museum, Yale. Some of the characters used to separate fossil Agrionines are so variable in recent species as to be of small value. This was pointed out to me by Dr. Calvert, and is very clearly indicated by a series of *Enallagma* very kindly given to me by Mr. E. B. Williamson. Thus:

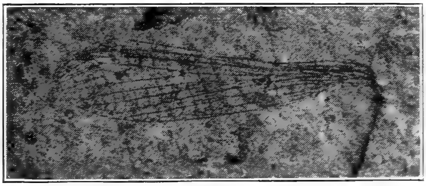

FIG. 2. *Enallagma florissantella.*

(1) Cells between M_1 and M_2 before doubling begins. A specimen of *E. antennatum* (*fischeri*) has three in anterior wing, four in posterior.

(2) Cells between quadrangle and level of nodus (supposed to separate the fossil *Agrion exsularis* Scudd. from *A. mascescens* Scudd., the first having three, the second four). Three is the usual number in *Enallagma*, but *E. traviatum* may have four, and in a male *E. carunculatum* one wing has four, the other three wings three each.

(3) Length of upper side of quadrangle. It is much shorter in anterior than posterior wings of *Enallagma civile*, *E. antennatum*, *E. exsulans*, and *E. traviatum*.

On the other hand, many undoubtedly distinct recent species are so similar in the wings that it is exceedingly difficult, to say the least, to separate them by these organs alone. In dealing with the fossils, therefore, one may well hesitate to assert that species are synonymous, although some of their assigned characters are likely to be of less than specific significance.

The Florissant species of this group may be separated as follows:

Subquadrangle with a cross-nervure in the middle; subnodus almost vertical; first postnodal cell considerably longer than second; eleven postnodal sectors. . . . .
"*Trichocnemis*" *aliena* Scudder.

Subquadrangle without a cross-nervure; subnodus oblique. . . . 1.

1. Nervures and stigma pale ferruginous; ten postnodal sectors; stigma very oblique, with the inner side as long as the outer. *Hesperagrion prævolans* Ckll.

Nervures dark brown or black; stigma ordinary. . . 2.

2. Costa before nodus conspicuously arched; 11 postnodal cross-veins; curved basal section of M_3 very short. . . *Agrion exsularis* Scudd.

Costa before nodus hardly arched; curved basal section of M_3 longer. . . . . 3.

3. Postnodal cross-veins 10 to 11; upper side of quadrangle longer than inner. *Agrion mascescens* Scudd.

Postnodals 14; upper side of quadrangle a little shorter than inner. *Enallagma florissantella* Ckll. (probably upper wing).

The postnodals in living *Enallagma* are from 9 to 11, at least in the species examined. I find the upper side of quadrangle much longer than inner in *E. fischeri* and *E. exsulans;* but in an upper wing of *E. carunculatum* the inner is longer than the upper. The difference between the quadrangles of *A. mascescens* and *E. florissantella* cannot be due to their representing different wings, for the upper wing of *mascescens* is known, and has the upper side of the quadrangle very long.

The position of the base of the quadrangle seems to be of some significance:

(1) Base of quadrangle conspicuously before level of midmost point between antenodal cross-veins. *A. mascescens.*

(2) Base of quadrangle at or near level of midmost point. *E. florissantella, A. exsularis, E. fischeri; E. signatum, E. hageni.*

(3) Base of quadrangle far beyond level of midmost point, not far from level of first cross-vein. *E. carunculatum, E. civile.*

Trichocnemis aliena Scudder. Figure 3.

A wing was obtained at Station 13 B (*W. P. Cockerell*). The most striking character, the crossed subquadrangle, is unfortunately not visible in our specimen, but there is no reason to doubt that it exists, as represented in Scudder's figure. Mr. Williamson writes:

"*Paraphlebia* is the only Agrionine genus known to me with crossed subquadrangle. It is a character that disappears with reduction in the Calopteryginæ; e. g., *Diphlebia* has it rarely crossed. *Cyanocharis* has quadrangle but not subquadrangle crossed; *Devadatta* has both quadrangle and subquadrangle crossed; *Micromerus* has quadrangle usually crossed and subquadrangle with one or two cross-veins. *Paraphlebia*, mentioned above, of course is entirely different from *Trichocnemis* in all other characters."

With regard to the vertical subnodus, Mr. Williamson writes: "*Xanthagrion erythroneurum* has it vertical; *Erythromma najas* (especially the hind wing) nearly or practically so; it is nearly vertical in the American *Oxyagrion*, *Argia*, *Hyponeura* and *Ischnura* (at least some of the species). This character, I believe, appears independently many times, and is no criterion in itself" of generic relationships.

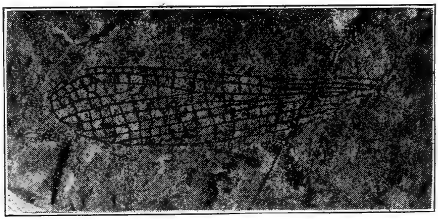

FIG. 3. *Trichonemis aliena.*

Except for the crossed subquadrangle, Mr. Williamson says that he sees no objection to referring *T. aliena* to *Hesperagrion*. "The form of wing is similar; the quadrangle, subquadrangle and the relations of their parts to the antenodals are similar; the origin of M_2 is similar; and the length and direction of the subnodus are not far out of the way. I believe, in this view, that *T. aliena* [Scudder's type] is a hind wing." Mr. Williamson further adds:

"I have compared Scudder's figure with wings of *Calicnemis*, *Hemicnemis* (*Leptocnemis*), *Platycnemis* and *Tatocnemis*,—some of the genera usually associated with *Trichocnemis*. If Scudder's figure of wing is correct in outline, *T. aliena* is not similar to any of the above genera. In arrangement of veins at distal end of quadrangle, *T. aliena* is most similar to *Hemicnemis* (which genus, of the whole group, has the quadrangle most dissimilar) and *Calicnemis*. In arrangement of veins at base of quadrangle it most resembles *Platycnemis*. Moreover, in above genera, only in *Platycnemis* is the subnodus nearly or quite vertical. In *Tatocnemis* (which is very dissimilar in many characters), the subnodus is very short."

Our specimen, like Scudder's, has eleven postnodal crossnervures. The first cross-nervure beyond the stigma is forked below. There are three cells between M_1 and M_2 before the doubling begins (four in Scudder's type). There is a very distinct brace-vein. The figured specimen is in Peabody Museum, Yale.

Hoplonæschna separata (Scudder).

Two specimens, representing the hind wing, were obtained at Station 14, one by my wife, the other by myself. Scudder's type, an anterior wing, was referred to *Basiæschna*; but Needham expressed the opinion that it belonged to *Hoplonæschna* (Pr. U. S. Nat. Mus., xxvi, p. 761). The new specimens are far from perfect, but they show that the hind wing has the following characters:

(1) Triangle with a double cell at base, and then four simple cells, varying to a double and three simple cells.
(2) Anal triangle of three cells.
(3) M_4, after running parallel with M_3, separated by a single row of cells, is suddenly bent downwards, and is separated by two and three rows of cells; a character of *Hoplonæschna*.

In my table in Bull. Amer. Mus. Nat. Hist., xxiii, pp. 133, 134, the insect runs to *Basiæschna*; but the anal triangle agrees with *Hoplonæschna*, and not so well with *Basiæschna*. On the other hand, as to the stigma *H. separata* is like *Basiæschna*, not like *Hoplonæschna*. The region about the triangle agrees almost exactly with *Gynacantha*.

The number of cells in the triangle is variable in *Æschnids*. Mr. Williamson, to illustrate this point, has very kindly sent statistics of three very closely allied forms of *Æschna*, based on males. In order to make them clear, I have constructed cell formulæ, enumerating the cells in order, beginning from the base. Thus 2, 1, 1, means a double cell and then two simple ones; 1, 1, 1, three cells, all simple.

Front Wing.

1, 1, 1, . . Indiana species (2 specimens).
2, 1, 1, . . *Multicolor* (seven).
2, 1, 1, 1, *Multicolor* (eleven), Indiana sp. (18), Jalapa sp. (7).
2, 2, 1, 1, *Multicolor* (two), Jalapa sp. (1).

Hind Wing.

2, 1, ... *Multicolor* (one).
2, 1, 1, . . *Multicolor* (17), Jalapa sp. (4), Indiana sp. (2).
2, 1, 1, 1, *Multicolor* (two), Jalapa sp. (4), Indiana sp. (18).

The number of cells in the anal triangle Mr. Williamson states is also not of generic importance. He adds: "The kink in M_4 is a character generally associated with the curving backwards of radial and median supplements (see *Coryphæschna ingens* for maximum of both characters, and *Nasiæschna*, e. g., for minimum)." Mr. Williamson concludes that *separata* cannot go in *Basiæschna*; and unless a new genus is proposed for it, *Hoplonæschna* seems to be the only genus to receive it.

Phenacolestes parallelus Ckll.

This species was described from the apical part of the wing. The base of a wing, probably belonging to *P. parallelus*, is from Station 14 (*Geo. N. Rohwer*). It differs from *P. mirandus* Ckll., in having six antenodal cross-nervures, the nervure from subquadrangle to lower margin arising from almost the apex of the former, and cross-nervure in fork of M_{1+2} and M_3 before level of nodus. The part visible (as far as separation of M_1 from M_2) is hyaline.

(10) *A Longicorn Beetle from Florissant.*

Saperda (?) *submersa* sp. nov. Figure 4.

Length about 22^{mm}; width of head about $4\frac{1}{2}$; width of thorax about 4; of insect in humeral region of elytra about $7\frac{1}{2}$; length of head and thorax about $6\frac{1}{2}^{mm}$; antennæ rather thick, probably about 16^{mm} long, but the extreme tip missing. Head dark above, but face and mouth pallid; thorax pallid, darker posteriorly; elytra black at base (especially on humeri), after which comes a broad (about $4\frac{1}{2}^{mm}$ long) light area, forming a broad band across both elytra, the remaining portion of the elytra black. Abdomen extending a little beyond tips of elytra.

4

In general build and appearance, this is like *Saperda*. I cannot demonstrate any lateral spines on thorax and believe there were none, but this part is not very clearly visible. The transverse light area on the elytra recalls *Oncideres cingulatus*, although more basal than in that insect; the antennæ are like those of *Saperda*, not like *Oncideres*. The rather broad head suggests *Mecas* rather than *Saperda*. Type from the Miocene shales of Florissant, Colorado, collector unknown. Mr. G. L. Cannon, who kindly placed it in my hands for description, informs me that it has been in the collection at the State Capitol for at least 25 years.

Four fossil species of *Saperda* have been described from Europe. Three are from the Miocene, but one of these (*S. valdensis* Heer) is not identifiable.

University of Colorado, Boulder.

Art. VII.—*New Fossil Elateridæ from Florissant:* by H. F. Wickham.

Corymbites Latr.

C. granulicollis (figure 1).—Body rather short and stout. Head about equal in length and breadth, front apparently transversely rugose; antennæ broken, but the remaining portion shows them to have been rather slender and only very little serrate, probably not attaining the hind angles of the thorax. Prothorax emarginate and narrower at apex, growing broader with equal lateral curve to about the middle, then arcuately narrowing to a point just anterior to the posterior angles, which are rather markedly divergent and distinctly unicarinate; the disk with small closely placed granules, each with a minute central puncture. These granules become much finer and more crowded near the sides, and a median basal area (which may have been canaliculate) is nearly devoid of them. Elytra finely alutaceous, finely and sharply striate but not punctured. Anterior leg (the only one visible) short, second, third and fourth tarsal joints about equal.

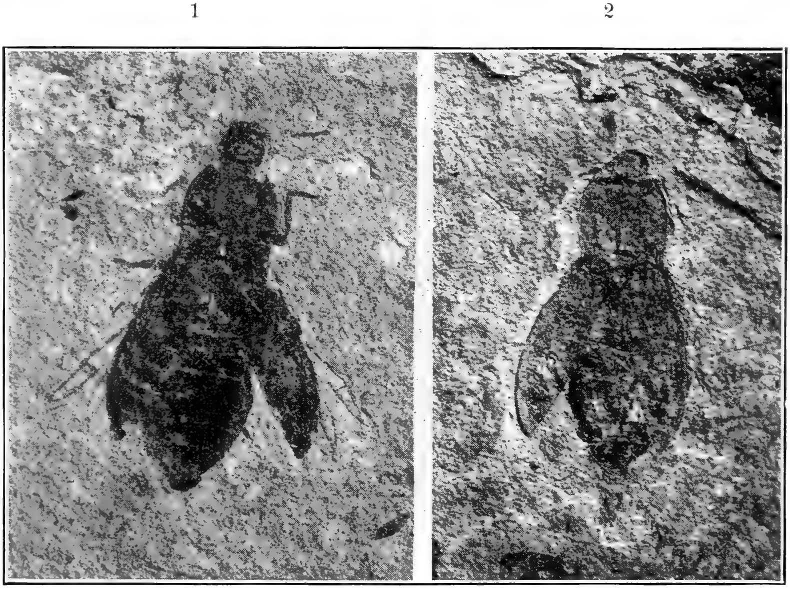

Fig. 1. *Corymbites granulicollis*, n. sp. × 2.
Fig. 2. *Corymbites primitivus*, n. sp. × 2.

Length (of entire insect) ·96 in., of elytron about ·60 in., of prothorax about ·23 in.; width of prothorax about ·26 in.

I place this insect in *Corymbites* from the general form; the shape of the prothorax strongly recalls that of *C. carbo* Lec., and *C. æreipennis* Kby.

One specimen (Cat. No. 1, Peabody Museum, Yale), Station 14; S. A. Rohwer.

C. primitivus (figure 2).—Form rather stout, head finely and rather closely punctured. Prothorax emarginate at apex, front angles obtuse, sides broadly arcuate, more sharply in front of the middle, the greatest width being at about one-third of the length, hind angles distinctly carinate but rather short and not strongly divergent; disk finely densely subrugosely punctate, less closely along the middle. Elytra with fine sharp impunctate striæ, interstitial spaces finely irregularly punctured. Legs and antennæ invisible.

Length, entire, ·87 in., of elytron ·50 in., of prothorax along median line ·20 in.; width of thorax ·23 in., of elytron about ·13 in.

One specimen (Cat. No. 2, Peabody Museum, Yale), Station 13; Geo. N. Rohwer.

Here, again, I have placed the species by its general appearance, the truly generic characters all being obscured.

Melanactes Le Conte.

M. cockerelli (figure 3).—Body moderately elongate. Head narrower than thoracic apex, antennæ attaining base of thorax, basal joints obscured, the seven distal ones subequal in width and but slightly serrate, each very little longer than wide, front fairly closely but not coarsely punctured. Prothorax slightly broader than long, narrowest at apex, arcuately wider to a point a little behind the middle, thence slightly narrowed to near the hind angles which are somewhat (but not markedly) divergent, disk finely and closely punctate towards the sides but much more sparsely and a trifle more coarsely about the middle; the marginal bead of the pronotum is very distinct, but it is uncertain whether the hind angles are carinate or not. Elytra apparently distinctly alutaceous, striate, the striæ fine and marked at their bottoms with rows of moderately deep slightly elongate punctures which are separated by intervals arranging approximately the lengths of the punctures. Legs invisible.

Length, entire, ·94 in., width of prothorax, slightly behind the middle, ·26 in., of elytron ·37 in.

One specimen (obverse and reverse, Cat. No. 3, Peabody Museum, Yale), Station 14; Mrs. W. P. Cockerell.

FIG. 3. *Melanactes cockerelli*, n. sp. × 2.

In life, this insect must have been about the size of *M. densus* Lec., or *M. piceus* De G., resembling the former very closely in thoracic and elytral sculpture.

Named after a good friend and ardent entomologist, Professor Cockerell, from whose hands the foregoing species were received.

Iowa City, Iowa.

ART. VIII.—*The Estimation of Iron and Vanadium in the Presence of One Another;* by GRAHAM EDGAR.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxvi.]

THE difficulties in the separation of vanadic acid from iron were early recognized. In 1877 Bettendorf* noted that ammonium hydroxide precipitates from a solution containing these substances a yellow vanadate of iron not entirely decomposed by an excess of the reagent. He therefore added an excess of ammonium phosphate and boiled the solution, whereby the iron was converted into ferric phosphate and precipitated as such on the addition of ammonium hydroxide, while the vanadium remained in solution. Carnot† used repeated precipitation by ammonium hydroxide, ammonium acetate or ammonium sulphide, this process serving to remove iron but not aluminium or chromium. According to Classen,‡ vanadic acid may be separated from iron in ores by fusion with sodium carbonate and sodium nitrate, and extraction of the melt with water, the vanadium going into solution as sodium vanadate. According to Arnold,§ in the analysis of steel, a fusion with sodium peroxide and extraction with water serves to obtain the vanadic acid in solution, free from iron. Fritcherle,‖ in the analysis of carnotite, precipitated iron together with uranium and vanadium with an excess of sodium carbonate, then added sodium hydroxide and boiled for some time, the vanadic acid alone going into solution. Blum,¶ in separating vanadium from rather large amounts of iron, as in pig iron, states that the separation is only complete when, after precipitation of the iron as hydroxide or basic acetate, the precipitate is redissolved, tartaric acid added and the iron precipitated by means of an excess of ammonium sulphide, the solution being allowed to stand for several hours. Campagne** separates the greater part of the iron in ferrovanadium and vanadium steel by repeated extraction of the hydrochloric acid solution with ether, afterward determining the vanadium by repeated evaporation with concentrated hydrochloric acid, removal of this acid by means of sulphuric acid, and titration with potassium permanganate. He states that if it be desired to determine the iron present, the original solution, without extracting with ether, may

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* Poggendorff's Ann. der Phy., clx., 126-131.
† Chem. News, lvi, 16
‡ Amer. Chem. Journal, vii, 349-353.
§ Electrochemist and Metallurgist, March-April 1902.
‖ Chem. News, lxxxii, 258.
¶ Zeitschr. Anal. Chem., xxxix, 156-157.
** Ber. der Dtsch. Chem. Gesel., xxxvi, 3164.

be boiled repeatedly with hydrochloric acid to reduce the vanadic acid, the hydrochloric acid removed by means of sulphuric, and the vanadium titrated with permanganate. If then the solution be reduced with hydrogen sulphide, the excess of gas removed by boiling and the solution again titrated with permanganate, the difference between the two titrations will give the iron present. Glasmann[*] effects the separation by adding potassium iodide to the sulphuric acid solution, removing the free iodine by means of sulphur dioxide, neutralizing with potassium hydroxide, and precipitating the iron by means of a mixture of potassium iodide and iodate. The liberated iodine is removed by sodium thiosulphate, the ferric hydroxide filtered off and the vanadium estimated in the filtrate.

Among other methods of separation may be mentioned that of Classen,[†] who precipitates the iron electrolytically from a solution of the double oxalates, and Myers,[‡] who deposits the iron using a mercury cathode, the vanadium in both cases remaining in solution.

In view of the difficulties attendant upon the separation of iron and vanadium, and in view of the increasing importance of such substances as ferrovanadium and vanadate of iron, composed almost entirely of these elements, it has been thought advisable to present a method by which vanadium and iron may be estimated in the presence of each other.

If a solution containing vanadic acid and iron be reduced by means of sulphur dioxide the reoxidation by potassium permanganate proceeds according to the equation

$$5V_2O_4+10FeO+4KMnO_4=5V_2O_5+5Fe_2O_3+2K_2O+4MnO \quad (1)$$

If this solution, after titration, be passed through a column of amalgamated zinc in the Jones reductor, the receiving flask being charged with a solution of ferric sulphate, the reduction is carried, in the case of vanadic acid, to the condition of V_2O_2[§] and the reoxidation by permanganate proceeds according to the equation

$$5V_2O_2+10FeO+8KMnO_4=5V_2O_5+5Fe_2O_3+4K_2O+8MnO \quad (2)$$

The difference in the number of cubic centimeters of permanganate used in the first and second titrations is evidently used in oxidizing the vanadium from the condition of V_2O_2 to V_2O_4, and multiplied by the factor ·00456 (for exactly N/10 solutions) gives the amount of vanadic acid present. This being known, the iron present may be calculated from the amount of permanganate used in either titration.

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[*] J. russ. Phys. Chem. Ges., xxxvi, 77.

[†] Ber. Dtsch. Chem. Ges., xiv, 2771–83.

[‡] J. Amer. Chem. Soc., xxvi, 1124.

[§] Gooch and Edgar, this Journal, xxv, 233.

In the experiments in Table I three standard solutions were used, viz.:—

1. A solution of potassium vanadate, slightly acidified with sulphuric acid, and containing 11·36 grams of vanadic acid to the liter. This solution was standardized by the method of Holverscheit.*

2. A solution of ferric alum, slightly acid, with sulphuric acid and containing 14·37 grams of ferric oxide to the liter. This solution was standardized by the very accurate method of Newton.†

3. An approximately tenth normal solution of potassium permanganate (3·16 grm. per lit.), standardized against a N/10 solution of arsenious oxide.

The details of manipulation were as follows:—Measured portions of the ferric sulphate solution were mixed with portions of the solution of vanadic acid, and a current of sulphur dioxide was passed through the slightly acid mixture until the color had changed from red into green and finally into a clear blue. A few centimeters of dilute sulphuric acid were then added, and the solution heated to boiling, the current of sulphur dioxide being replaced by one of air-free carbon dioxide. When the last traces of sulphur dioxide had been removed, the flask was cooled in running water, the atmosphere of carbon dioxide being maintained, and when thoroughly cool, titrated with potassium permanganate until the color had changed from blue into yellowish green. The solution was then heated to

Ferric Alum in Receiver 10% cm³.	I KMnO$_4$ N/10 × 9545 cm³.	II KMnO$_4$ N/10 × 9545 cm³.	V$_2$O$_5$ taken grm.	V$_2$O$_5$ found grm.	Error on V$_2$O$_5$ grm.	Fe$_2$O$_3$ taken grm.	Fe$_2$O$_3$ found grm.	Error Fe$_2$O$_3$ grm.
35	31·90	58·02	0·1136	0·1137	+0·0001	0·1437	0·1436	−0·0001
35	31·90	58·04	0·1136	0·1138	+0·0002	0·1437	0·1435	−0·0002
35	31·85	58·00	0·1136	0·1138	+ ·0002	0·1437	0·1433	−0·0004
35	31·90	58·00	0·1136	0·1136	±0·0000	0·1437	0·1437	±0·0000
20	25·30	38·35	0·0568	0·0568	±0·0000	0·1437	0·1423	−0·0004
20	25·29	38·30	0·0568	0·0566	−0·0002	0·1437	0·1433	−0·0004
20	15·98	29·02	0·0568	0·0568	±0·0000	0·0719	0·0721	+0·0002
50	38·50	77·60	0·1704	0·1702	−0·0002	0·1437	0·1442	+0·0005
50	38·45	77·60	0·1704	0·1704	±0·0000	0·1437	0·1438	+0·0001
50	38·45	77·58	0·1704	0·1703	−0·0001	0·1437	0·1439	+0·0002
35	22·50	48·60	0·1136	0·1136	±0·0000	0·0719	0·0720	+0·0001
35	22·50	48·60	0·1136	0·1136	±0·0000	0·0719	0·0720	+0·0001
35	22·45	48·58	0·1136	0·1137	+0·0001	0·0719	0·0716	−0·0003
20	15·97	29·07	0·0568	0·0570	+0·0002	0·0719	0·0718	−0·0001

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* Inaug. Diss., Berlin, 1890.

† This Journal, xxv, 343.

70°–80° and the titration completed at that temperature. The solution, having now a volume of 100–150$^{cm^3}$, was passed through a column of amalgamated zinc in a long Jones reductor, being preceded by 150$^{cm^3}$ of hot dilute (2½ per cent) sulphuric acid and followed by 100$^{cm^3}$ of dilute acid and finally 200$^{cm^3}$ of distilled water. The receiving flask, containing an excess of ferric sulphate, was kept cool by means of running water, and its contents, after the addition of sirupy phosphoric acid to remove the color of the iron, were titrated with permanganate until the color had changed from bluish green to yellow, and the color of the permanganate began to be persistent and destroyed only by shaking. The flask was then heated to 70°–80° and the titration completed in the hot solution.

The results given in the table show that iron and vanadium may be readily estimated in the presence of each other by two oxidations with potassium permanganate, following reduction first with sulphur dioxide and last with amalgamated zinc, under the conditions described above.

In conclusion, the author desires to thank Prof. F. A. Gooch for advice given in the course of the work.

ART. IX.—*On the Estimation of Cerium in the Presence of the other Rare Earths by the action of Potassium Ferricyanide;* by PHILIP E. BROWNING and HOWARD E. PALMER.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxvii.]

THE work to be described was undertaken to determine how completely the oxidation of cerium from the cerous to the ceric condition may be effected by potassium ferricyanide in alkaline solution, and how completely the measure of the oxidation can be registered in the amount of potassium ferrocyanide formed, according to the following equation:

$$2K_3FeC_6N_6 + Ce_2O_3 + 2KOH = 2K_4FeC_6N_6 + H_2O + 2CeO_2.$$

For this work a solution of pure cerous sulphate was made and standardized by precipitating measured and weighed portions with a definite amount of a standard solution of sodium oxalate, filtering, igniting the cerium oxalate, and weighing the ceric oxide obtained. As a check on this method, the excess of the sodium oxalate over the amount used for the precipitate was determined in the filtrate by titration with potassium permanganate, and this amount was subtracted from the whole amount of sodium oxalate used. From this result the cerium present can be readily estimated, the amount of sodium oxalate used in the precipitation being known.*

The ferricyanide solution used was made by dissolving 2 grams of carefully selected crystals of potassium ferricyanide in 100^{cm^3} of water. About 20^{cm^3} of this solution were used in each determination.

The procedure was as follows: To measured and weighed portions of the cerous sulphate solution 20^{cm^3} of the ferricyanide solution were added, and potassium hydroxide in solution to complete precipitation.

The precipitated hydroxide was filtered off and the filtrate and washings, amounting in volume to from 200^{cm^3} to 250^{cm^3}, after being made distinctly acid with dilute sulphuric acid, were titrated with a standard solution of potassium permanganate until the presence of the permanganate color showed the oxidation of the ferrocyanide to the ferricyanide,† according to the equation:

$$5K_4FeC_6N_6 + KMnO_4 + 4H_2SO_4 = 5K_3FeC_6N_6 + 3K_2SO_4 + MnSO_4 + 4H_2O.$$

By this equation and the preceding one the amount of cerium present can be readily calculated.

Each day before the ferricyanide was used a portion of 20^{cm^3} of the solution was acidified and titrated with the permanganate to color, and the amount necessary, generally from one to three drops, was subtracted from the amount of the perman-

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* Browning and Lynch, this Journal [4], viii, 457, 1899.

† Sutton's Volumetric Analysis, IX edition, page 209.

ganate used in the actual determination. It is of interest to note that ferricyanide solutions kept in clear glass bottles for a week or more showed variations of only a drop or two in the amount of permanganate taken up.

All the various operations in this process were carried on without warming the solution. The filtrations and washings were generally made under gentle pressure, and required on an average not more than fifteen to thirty minutes. In Table I the results obtained with cerium present alone are given.

TABLE I.

	Ce taken, calculated as Ce_2O_3 grm.	Ce found, calculated as Ce_2O_3 grm.	Error grm.
(1)	0·1834	0·1819	—0·0015
(2)	0·1376	0·1380	+0·0004
(3)	0·1834	0·1829	—0·0005
(4)	0·1834	0·1829	—0·0005
(5)	0·1834	0·1834	+0·0000
(6)	0·1376	0·1385	+0·0009
(7)	0·1376	0·1371	—0·0005
(8)	0·1376	0·1374	—0·0002
(9)	0·1376	0·1380	+0·0004
(10)	0·1834	0·1824	—0·0010
(11)	0·1326	0·1335	+0·0009
(12)	0·1326	0·1328	+0·0002

Solutions of the salts of the other rare earths, containing about 0·1 grm., were treated by the same method, and the failure to obtain evidence, by the permanganate, of the formation of potassium ferrocyanide, showed that there is no oxidation of these salts by the ferricyanide.

In Table II the results obtained by estimating cerium according to this method in the presence of the other rare earths are given.

TABLE II.

	Ce taken, calculated as Ce_2O_3 grm.	Ce found, calculated as Ce_2O_3 grm.	Error grm.	Other Rare Earths present, calculated as oxides grm.
(1)	0·1328	0·1335	+0·0007	0·1 ThO_2
(2)	0·1327	0·1322	—0·0005	0·1 "
(3)	0·0266	0·0275	+0·0009	0·1 "
(4)	0·0267	0·0272	+0·0005	0·1 "
(5)	0·1324	0·1326	+0·0002	0·1 Y_2O_3
(6)	0·1326	0·1323	—0·0003	0·1 "
(7)	0·0266	0·0264	—0·0002	0·1 "
(8)	0·0264	0·0271	+0·0005	0·1 "
(9)	0·1376	0·1370	—0·0006	0·15 $La_2O_3 + Di_2O_3$
(10)	0·1101	0·1091	—0·0010	0·15 " "
(11)	0·1324	0·1332	+0·0008	0·03 ZrO_2

This method presents no difficulties in manipulation and is especially adapted to the rapid estimation of cerium in rare earth mixtures.

ART. X.—*The Estimation of Chromium as Silver Chromate;* by F. A. GOOCH and L. H. WEED.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxviii.]

IT has been shown by Autenrieth* that when chromic acid is added to a boiling solution of silver nitrate, or when a soluble chromate or dichromate is added to a solution of silver nitrate previously acidified with nitric acid, or when silver chromate is treated with nitric acid, silver dichromate is formed; and that, on the other hand, it is silver chromate which is precipitated when silver nitrate in excess is added to a solution of a soluble dichromate, cold or hot, the reaction proceeding according to the equation

$$4AgNO_3 + K_2Cr_2O_7 + H_2O = 2Ag_2CrO_4 + 2KNO_3 + 2HNO_3.$$

The characteristics of both silver dichromate and silver chromate have recently been summarized and further studied by Margosches,† but so far as we know there is in the literature no account of procedure for the exact quantitative determination of either chromium or silver based upon the characteristics of either of these salts. The solubility of silver dichromate in water and in ordinary solutions is such as to preclude the use of this substance as the final product of a quantitative process depending upon precipitation. The solubility of silver chromate in a moderately large volume of water is not inconsiderable, and the solvent action of free acid, even acetic acid in quantity, is marked. We have found, however, that the precipitation of silver chromate is practically complete in a solution only faintly acid with acetic acid and in presence of a large excess of silver nitrate. If such a precipitate is collected in the filtering crucible and washed with a dilute solution of silver nitrate, until no other impurities remain, silver chromate does not dissolve, and the excess of silver nitrate may be removed by the cautious use of water without appreciable effect upon the precipitate. The present paper has to do with the determination of chromium as silver chromate.

In the experiments of which the details are given in the table, the general treatment just described was put to the practical test. Given amounts of potassium dichromate were weighed out and dissolved in hot water, as in experiments (11) and (12), or given amounts of a solution of potassium dichromate of known strength were run from a burette into a beaker and heated to boiling, as in experiments (1) to (10). To the hot solution of the dichromate was added, drop by drop, a

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* Ber. Dtsch. chem. Ges., xxxv, 2057.

† Zeitschr. anorg. Chem., xli, 68; l, 231.

solution of silver nitrate in considerable excess, and the mixture was again brought to the boiling point. Ammonium hydroxide was added until the clear liquid became colorless and turned litmus paper blue; then acetic acid was added cautiously until the reaction of the solution was distinctly acidic to litmus. After standing for at least a half hour the precipitate was filtered off on asbestos in a perforated crucible, washed first with a dilute solution of silver nitrate and then with 20^{cm^3} to 30^{cm^3} of distilled water applied in small portions, and dried with gentle heating to a constant weight. In experiments (1) to (10), the drying was done in an air bath heated to 135°; in experiments (11) and (12), the crucible and precipitate were heated gently over the free flame. In experiments (7) and (8) the precipitation was made in presence of 5 grms. of ammonium nitrate, and in (9) and (10) in presence of 5 grms. of sodium nitrate, to test the effect of each of these substances upon the process. In no case did the filtrate, with the washings, show by the lead acetate test the presence of a chromate.

The Precipitation of Silver Chromate.

	$K_2Cr_2O_7$ taken grm.	$AgNO_3$ Used in precipitation grm.	Volume at precipitation cm^3.	Ag_2CrO_4		
				Found	Theory	Error
(1)	0·0921	0·4248	100	0·2072	0·2076	—0·0004
(2)	0·0921	0·4248	100	0·2073	0·2076	—0·0003
(3)	0·0921	0·4248	100	0·2075	0·2076	—0·0001
(4)	0·0921	0·4248	100	0·2074	0·2076	—0·0002
(5)	0·0921	0·4248	100	0·2075	0·2076	—0·0001
(6)	0·0921	0·4248	100	0·2073	0·2076	—0·0003
(7)	0·0921	0·4248	100	0·2073	0·2076	—0·0003*
(8)	0·0921	0·4248	100	0·2075	0·2076	—0·0001*
(9)	0·0921	0·4248	100	0·2080	0·2076	+0·0004†
(10)	0·0921	0·4248	100	0·2070	0·2076	—0·0006†
(11)	0·5801	3·	150	1·3087	1·3082	+0·0005
(12)	0·7352	3·	200	1·6573	1·6574	—0·0001‡

* The precipitation was made in presence of 5 grm. of NH_4NO_3.
† The precipitation was made in presence of 5 grm. of $NaNO_3$.
‡ An excess of 1^{cm^3} of 40% acetic acid was added before filtering.

From the results of these experiments it is apparent that accurate determinations of chromium taken as the chromate or dichromate may be secured by precipitating silver chromate in presence of an excess of silver nitrate, making the solution ammoniacal and then faintly acid with acetic acid, transferring the precipitate to the filtering crucible, washing with a dilute solution of silver nitrate, and, after other soluble impurities have been removed, finishing the washing with small amounts of water applied in successive portions.

Art XI.—*Note on the Standardization of the Fog Chamber by the aid of Thomson's Electron;* by Carl Barus.

1. *Advantages.*—Of all the methods which I have tried to evaluate the coronas in terms of the number of nuclei which they represent under given conditions of exhaustion, the above method is the most promising and expeditious. A single experiment need take but a few minutes. Incidentally the observer learns whether the negative and positive ions have both been captured; for on using the tables of coronas which I developed heretofore, the value of e may be computed, and the result must coincide with Thomson's value.

2. *Method.*—My first experiments were made with a metal plate in a fog chamber, both the coronas and the current being observed successively, without changing the adjustment. But this was abandoned for a method in which a cylindrical condenser is employed as follows. A *closed* aluminum tube, $\cdot 62^{cm}$ in diameter 18^{cm} long, containing weak radium equally distributed along its inside, is made the core of a cylindrical condenser, $2\cdot 1^{cm}$ in external diameter, and leaded to an inch or more in thickness beyond. The aluminum core in question is suspended axially from a fine wire leading to a sensitive electrometer. The voltages here to be measured must of course be small, and hence all connecting wires are to be inclosed in earthed metal pipes.

The core in question is then removed from the electrical condenser and put into the axis of a dust-free fog chamber where the nucleation (ionization) is found on condensation from the contents of the corona; or vice versa. Here there are some outstanding difficulties; for the coronas are not the same throughout the length of the fog chamber. Even immediately around the radium core a single corona may be green on one side and red on the other. In a fog chamber 45^{cm} long, the coronas may vary from the glass end to the metal end of the chamber, in a way to correspond to from 100,000 to 200,000 nuclei, respectively, while the radium core is fixed in the middle. Inferring secondary radiation, one might naturally expect to obtain still larger coronas near the metal end, if the radium core (thoroughly sealed) is placed there, instead of in the middle of the chamber; but this is not the case, the coronas being markedly smaller than before, decreasing uniformly in size, however, toward the glass end. As the sealed aluminum tube is within the chamber, this behavior is puzzling and needs farther explanation. It is clearly of grave importance.*

These difficulties are inherent in the phenomenon and merely exhibited by the fog chamber. The latter has the great advantage that enormous nucleations, like millions per cubic centimeter, are not excluded. Under these circumstances the coronas alone are available for finding the nucleation inasmuch as nearly all the particles evaporate before subsiding.

3. *Preliminary Data.*—To test the efficiency of the fog chamber it is necessary to make a preliminary measurement of Thomson's e. Let the radii of the electrical condenser be R_1 and R_2 and its length l; let C (electrostatic units) be the capacity of the electric system (condenser and electrometer, together with such auxiliary capacity as may be inserted to get a leakage of proper value); let U be the combined velocity of the ions in a field of one volt per cm., V the voltage and $\dot{V}$ the change of voltage per second; finally let N be the nucleation given for the identical condenser core when placed in the fog chamber. Then for the cylindrical condenser (if natural logarithms be taken)

$$e = (C\dot{V} \ln R_1/R_2)/(600\,\pi l U V N).$$

If V is small enough to keep $\dot{V}/V$ constant, the curves show this at once. Rough tests using the old data of my fog chamber led to values of about as follows, when $C = 130$cm; $U = 3{\cdot}2$cm/sec.; V the fraction of a volt (less than one-half) and the field ·7 volts/cm.

$\dot{V}/V = {\cdot}050$ $N = 185{,}000$ $e \times 10^{16} = 3{\cdot}7$ electros. units
$\dot{V}/V = {\cdot}060$ $N = 210{,}000$ $e \times 10^{10} = 4{\cdot}3$ " "

The irregularities here are in the electrometer, as the connecting wires were not at the time surrounded by earthed pipes. On enclosing these, there was less irregularity, though the current was not quite proportioned to the voltage even for the low values of the latter. In a field of volt/cm, $V = {\cdot}7$, $\dot{V}/V = {\cdot}040$, $N = 150{,}000$ $10^{10} \times e = 3{\cdot}8$ were obtained. When the condenser was disconnected there was no leakage, showing the piping to be nearly free from such currents as might result from irregular penetration of the gamma rays.

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* As the radium is moved from the glass end to the brass end of the long fog chamber, the corona of maximum diameter (maximum nucleation) moves at a greater rate in the same direction; so that with radium in the middle, the maximum nucleation is already at the brass end, and then diminishes. It is surprising to notice the largest corona in the middle of the chamber, before the radium gets there. It is also possible to produce minimum of nucleation in the middle. The maximum rarely coincides with the position of the radium. Beta and gamma rays are alone active in these curious conflicts of primary and secondary streams.

With still higher nucleations $N = 570{,}000$ the data were $\dot{V} = \cdot 123$ volts, $V = \cdot 90$ volts, the field being 1·2 volts per cm, $\dot{V}/V = \cdot 137$ and $10^{10}\, e = 3\cdot 4$ electrostatic units. Thus it follows that both positive and negative ions must have been caught in the fog chamber.

4. *Other Equations.*—The available equations if I be the electrical current in the condenser, for which the nucleation in the annular volume v is n, while N is the nucleation in the fog chamber without current, b being the coefficient of the decay, are (apart from secondary radiation)

$$-\dot{n} = b(N^2 - n^2) - I/ev, \qquad (1)$$

$$I = C\dot{V}, \qquad (2)$$

where C is the capacity of the system,

$$I = 2\pi ln\, U V e/(\log R_1/R_2) \qquad (3)$$

where $\dot{V}/V$ is constant for very small voltages. Hence there would be a second method of reaching e in terms of b, or the reverse, if equation (1), where I is essentially a function of time, were integrable. Nevertheless the equation is available at once if V is large enough to make the current constant. In this case one may write, if N nuclei are found in the fog chamber without electrical current, while n occur in the condenser with current,

$$e = C\dot{V}/\left(300\pi(R_1^2 - R_2^2) lb(N^2 - n^2)\right).$$

Here n must be negligible compared with N. Values so obtained (an Exner graduated electroscope suffices) are quite consistent among themselves; but the data come out 20 to 30 too large if $b = 1\cdot 1 \times 10^{-6}$ is assumed.

Installing a plate condenser in the fog chamber, I noticed that for a charge of 100 or 200 volts the coronas between the condenser plates were of about the same character as the coronas without, while the large chamber is filled with ions at the highest voltages. Possibly therefore such ionization as reaches the inside of a condenser by diffusion may account for the excessive currents; or there may be increased production due to secondary radiation. It is interesting to note that potentials of 100 to 200 volts are sufficient to eject dust particles from the condenser, very small and not numerous it is true, but sufficient to make it possible to catch all the ions only after these dust particles have been precipitated in one or more exhaustions.*

5. *Conclusion.*—The good values of e obtained under widely varied conditions in the present very rough experiments, show that the present method is not unworthy of development, with a view to the further measurement of this

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* The complicated conditions encountered here will be restated elsewhere.

important constant. For this purpose I am at work on a redetermination of the nucleation values of the coronas, using as a source of light the virtually monochromatic mercury lamp. This is sufficiently intense and the coronas admit of the more definite optical interpretation.

Elsewhere* I pointed out that for large coronas the greater part of the fog particles evaporate; thus even at $n = 200,000$ particles per cubic cm., about one-half evaporate and one-half subside. Hence the corona method is here alone available for counting particles. I also showed that in the case of coronas the interference phenomenon superposed on the diffraction phenomenon may be treated in a way similar to the lamellar grating, consisting of alternate strips of thin and thicker transparent glass; that the given types of coronas must follow each other in the ratio of 5, 4, 3, 2, 1, 0 for their particle diameters and an increasing size of coronas; that the ratio of fog particle diameter and interference plate thickness, d/D, for the same color minimum in the interferences is $d/D = n/(n-1)$, where n is the refractive index, or about 7 to 8 in both cases. It must therefore be possible to compute the nucleation corresponding to a given corona at a given exhaustion and temperature, purely from optical considerations of diffraction and interference, as indicated. I hope to report the results in the near future.

Brown University, Providence, R. I.

* This Journal, xxv, p. 409, 1908.

† Ibid., p. 224, 1908.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *Volumetric Method for Chlorates.*—The best known volumetric processes for determining chlorates are the iodometric method and the method depending upon the oxidation of a ferrous salt. The latter is the more rapid of the two, and it has been extensively employed. To complete this reaction, however, boiling for about ten minutes is necessary. **Knecht** has recently described a new method for this determination, based upon the use of titanous chloride for the reduction. This reagent acts more rapidly than a ferrous salt, so that no heating is required. The procedure is as follows: 50^{cc} of standard titanous chloride solution (of which $1^{cc} = \cdot 0015^{g}$ of iron or thereabouts) are run into 5^{cc} of concentrated hydrochloric acid contained in a conical flask through which a current of carbon dioxide is maintained. Then 10^{cc} of the chlorate solution (1^{g} in 500^{cc}) are added. After a lapse of not less than three minutes, potassium sulphocyanide is added, and the excess of titanous chloride estimated by titration with iron alum solution until a permanent red color is obtained. For the estimation of chlorate in bleaching powder the available chlorine due to hypochlorite is estimated in the usual way by adding potassium iodide and starch and titrating with hydrosulphite in the presence of acetic acid. A second portion of the solution is then titrated with titanous chloride, the result giving total chlorine from hypochlorite and chlorate.—*Jour. Soc. Chem. Industry*, 1908, 434. H. L. W.

2. *Atomic Weight of Radium.*—Mme. Curie's first determination of this atomic weight gave the number 225. Subsequently she obtained with a larger amount of material (about four decigrams of radium chloride) the higher number 226·2. T. E. **Thorpe** has now repeated the determination of this interesting constant, and has obtained three results, 22.68, 225·7, and 227·7, which agree satisfactorily with those of Mme. Curie, although he used a much smaller amount of radium chloride, only 6 or 8 centigrams, for the determinations. Both investigators have used the same principle, the comparison of the weight of radium chloride with that of the silver chloride produced from it by precipitation. To avoid losses by transferring, Thorpe made use of small glass-stoppered flasks for all of the operations—weighing the radium chloride, dissolving it, precipitating with silver nitrate, washing the silver chloride by decantation, and drying and weighing in a single flask. Spectroscopic evidence is given that the radium chloride was free from all but the minutest traces of barium. It had been very carefully purified by the usual course of fractional crystallization. There are several circumstances which may affect the determination of the atomic

weight of radium. Thorpe states that the chloride gradually increases in weight when exposed to the air, apparently on account of oxidation by ozone, the presence of which can be perceived by the odor, and by other tests. Another peculiarity of the radium salt is its action upon the vessels containing the solution. It gradually changes the color of colorless rock crystal vessels to deep purplish black, and these as well as porcelain and glass vessels appear to be slightly attacked chemically with the formation of silicates.—*Chem. News*, xcvii, 229. H. L. W.

3. *The Polyiodides of Potassium, Rubidium, and Caesium.*—Using solubility methods, together with analyses of the undissolved residues, FOOTE and CHALKER have determined the polyiodides of potassium, rubidium, and caesium existing at 25°, and have found positive evidence of the existence of KI_3, KI_7, RbI_3, CsI_3, and CsI_5, while they found no evidence whatever of the existence of RbI_7, RbI_9, CsI_7 and CsI_9 which had been supposed to exist by Abegg and Hamburger, who used somewhat similar physical methods, but did not analyze the residues. It is to be noticed, also, that Abegg and Hamburger did not find KI_3, the first of these compounds that was discovered. It appears that while Abegg and Hamburger's work was correct in principle, there must have been some irregularity in their solubility determinations, leading to incorrect conclusions.—*Amer. Chem. Jour.*, xxxix, 561. H. L. W.

4. *A Volumetric Method for Copper.*—A process based upon the titration of cuprous thiocyanate with potassium iodate solution in the presence of strong hydrochloric acid has been worked out by JAMIESON and others of the Sheffield Scientific School. The reaction corresponds to the equation $4CuSCN + 7KIO_3 + 14HCl = 4CuSO_4 + 7KCl + 7ICl + 4HCN + 5H_2O$. The titration is carried out in a glass-stoppered bottle with a liquid containing about half of its volume of concentrated hydrochloric acid in the presence of a little chloroform. The disappearance of the iodine color in the chloroform marks the end of the reaction, and it is exceedingly sharp and delicate. The presence of filter paper does not affect the result. This general method of titration is due to L. W. Andrews, but it was not applied by him to thiocyanates, to which it has now been found to be applicable. The authors give details for applying the method to copper ores and alloys in such a way as to remove interfering substances. Test analyses showed excellent results, and the method appears to be a very rapid and accurate one.—*Jour. Amer. Chem. Soc.*, xxx, 760. H. L. W.

5. *Thermodynamics of Technical Gas-Reactions;* by F. HABER. Translated by Arthur B. Lamb. 8vo, pp. 356. London and New York, 1908 (Longmans, Green & Co.).—This book consists of a series of seven lectures which have been considerably enlarged for publication. The mechanical theory of heat is developed, as the author says, from its very foundations. Then a number of reactions, which are important industrially, are treated from a theoret-

ical standpoint in a very thorough manner. The lectures are: (1) The latent heat of chemical reaction and its relation to reaction energy; (2) and (3), Entropy and its significance in gas reactions. (4) Examples of reactions which proceed without a change in the number of molecules. (5) Some examples of reactions involving a change in the number of molecules. (6) Determination of the specific heat of gases. (7) Determination of gaseous equilibrium, with a theoretical and technical discussion.

H. W. F.

6. *A Search for Fluctuations in the Sun's Thermal Radiation through their Influence on Terrestrial Temperature;* by SIMON NEWCOMB. Trans. Amer. Phil. Soc., xxi, pp. 309–387.—The problem of variations in solar heat radiation as affecting terrestial temperatures is discussed in a thorough, impartial way in this memoir. The conclusions are none the less interesting because essentially negative in character, although the observations made by Langley and later at the Astrophysical Observatory at Washington have seemed to indicate a different result. Newcomb shows that a careful study of the annual departures of temperature over many regions in equatorial and middle latitudes, indicate a fluctuation corresponding with the period of solar spots. The maximum fluctuation, however, for tropical regions is only 0·13° C., or, in other words, the amplitude of the change is 0·26° C., less than one-half degree Fahrenheit. The corresponding fluctuation of the sun's radiation is, hence, concluded to be 0·2 of 1 per cent on each side of the mean. In addition, there is some inconclusive evidence of changes having a period of about six years, which may be plausibly attributed to changes in solar radiation. Apart from these changes the evidence at hand indicates that solar radiation is subject to no change producing a measurable effect upon terrestrial temperature; the magnetic, electric, and radio-active emanations may be left out of account, as their thermal effect is inappreciable. The ordinary terrestrial phenomena of temperature, rainfall and winds are thus uninfluenced by changes in the sun's radiation. That wide changes of temperature may occur, as those noted in 1903, when the temperature in Russia and Siberia, for example, was more than 20° F. above the normal, is interesting, but it is argued that these fluctuations cannot be attributed to changes in the radiation from the sun, because they do not extend to regions (i. e. the equatorial) where such changes would have their greatest effect.

II. GEOLOGY.

1. *Early Devonic History of New York and Eastern North America*; by JOHN M. CLARKE. N. Y. State Museum Mem., IX, pp. 366, pl. 48+. Albany, 1908.—To the important series of New York State Museum publications is now added the sumptuous memoir bearing this title, the peer of a notable line of predecessors and decidedly the crowning achievement on the part

of one of James Hall's most distinguished pupils. Critics are sparing nowadays in bestowing the terms monumental upon a scientific treatise, the adjective so often savors of hyperbole; and yet in the present case it must be allowed that any less superlative epithet would fail to denote the high character of Dr. Clarke's *magnum opus.* Space is here lacking for an adequate estimate of its contents, and the reviewer is perforce confined to a general appreciation.

The work is first of all a vast repository of information on a singularly complex subject, embracing great wealth of detail. To the practical student also, it commends itself as a digest in which all the essential facts of its theme are collected, classified, analyzed and interpreted with scrupulous exactness. Finally, the net result is systematized with the critical poise and acumen that mark the experienced investigator who brings to his task a broad grasp of cosmic problems, and whose mental attitude has been determined by the successful conquest of a large group of nature's secrets. The book betokens all these qualities and more; for on the humanistic side one is delighted by the literary skill with which the author handles his material, besides many a brilliant discursus on manners, customs, history, scenery, of an enchanting region. Naturally, as the title indicates, the chief objective aims of the memoir consist in a presentation of the essential features of the geology and paleontology of that time-interval in the Paleozoic of eastern North America with which our author is perhaps the most familiar, and on which he is recognized at home and abroad as an accomplished master. More particularly it deals with the origin and relations of the Lower Devonian rocks of Gaspé peninsula, with an elaborate discussion of their fossil remains, an investigation for which the author's earlier researches on the Guelph and Naples faunas of New York State served as a fitting prelude.

This volume is the fruit of several years of thoughtful study and patient effort, and it may be safely said that a work of this kind will never be superseded. And yet, such are the manifold resources and complexity of his material that the author assures himself and his readers that "the facts here brought together are but suggestions for further study of this fertile field." In this connection there comes to mind a German saying: "Wir sind alle Schuldner unserer Vorgänger," for in speaking of earlier workers Dr. Clarke pays a generous tribute to the memory of Logan, Billings, Dawson and other pioneer heroes of the Canadian Survey. Of Sir William's *Geology of Canada* it is said: "To a student of Gaspé geology, this is the compendium and guide." And with reference to *Palaeozoic Fossils* we find this: "It is our good fortune to be able to cite this work so frequently that our pages may almost seem its memorial." Yet we fancy that these twain explorers who handed along the torch are the very ones who would be most surprised at the large increment of knowledge and perfection of method that are signalized by the hand-some volume before us, illustrated by its beautiful lithographs and numerous full-page illustrations, several of which are in polychrome and most excellently done. Among paleontologists Plates *A* and *B* will command attention from being camera drawings by the author that recall his previous illustration of Dictyospongia in Memoir 2 of the same series.

One hundred pages of letterpress are devoted to an exploitation of the geology and physiography of Gaspé, this part being a substantial elaboration of the author's preliminary sketch of the geology of Percé (published in the Report for 1903), and the remainder of the volume consists of a technical discussion of the Gaspé invertebrate faunas. Upwards of 70 new species are described, and the characters of others are redefined. Especial interest attaches to the author's discussion of the origin, distribution and relations of Lower Devonic faunas, and the lines of their dispersal and invasion over different areas, this phase of the subject being treated with great ingenuity, and displaying keen philosophical judgment. It is to be noted, for instance, that the origin of the Gaspé sandstone is explained on the theory that it "was an Old Red lake in the same sense as those of Scotland and that in which the Oneonta and Catskill sands of New York were laid down." Due prominence is given to the fact that late stages of the Oriskany betray a large percentage of incoming migrants which form, as it were, the advance guard of the next organic invasion. Dr. Clarke accordingly concludes that the original determination of the age of the Gaspé beds as practically equivalent to the Oriskany of New York is insufficient, and he is able to trace a passageway by which the Hamilton contingent of this fauna entered the region from the Appalachian gulf, moving eastward amid lagoon conditions along the Atlantic border and thence into western Europe. This whole matter is admirably summarized at pages 250–252, and as the work is one that requires to be consulted by all students of the Devonian era, we cannot do better than recommend the reading of this section and others germane to it at first hand. C. R. E.

2. *Publications of the United States Geological Survey.*—Recent publications of the U. S. Geological Survey are noted in the following list (continued from vol. xxv, p. 150):

Topographic Atlas.—Sixty-five sheets. The sheets, 38 in number, embracing Connecticut with portions of the adjacent States have been collated and bound in a permanent volume which will be of great value to those interested in the region named. These volumes have been distributed by Congressman Lilley, the plan having originated with R. W. Thompson, private secretary to Senator Hawley. Bulletin No. 117 is bound in with the volume.

Folios.—No. 154. Winslow Folio, Arkansas—Indian Territory. Description of the Winslow Quadrangle; by A. H. Purdue. Pp. 6, with 3 maps.

No. 155. Ann Arbor Folio, Michigan. Description of the Ann Arbor Quadrangle; by I. C. Russell and Frank Leverett. Pp. 15, with 3 maps.

No. 156. Elk Point Folio, South Dakota,—Nebraska—Iowa; Description of the Elk Point Quadrangle; by J. E. Todd. Pp. 8, with 3 colored maps.

No. 158. Rockland Folio, Maine; by Edson S. Bastin. Pp. 15, with 5 colored maps.

Bulletins.—No. 319. Summary of the Controlling Factors of Artesian Flows; by Myron L. Fuller. Pp. 44, with 7 plates and 17 figures.

No. 325. A Study of Four Hundred Steaming Tests made at the Fuel-Testing Plant, St. Louis, Mo., in 1904, 1905, and 1906; by Lester P. Breckenridge. Pp. 196, with 76 figures.

No. 326. The Arkansas Coal Field; by Arthur J. Collier, with Reports on the Paleontology by David White and G. H. Girty. Pp. vi, 158, with 6 plates and 29 figures.

No. 327. Geologic Reconnaissance in the Matanuska and Talkeetna Basins, Alaska; by Sidney Paige and Adolph Knopf. Pp. 71, with 4 plates and 4 figures.

No. 328. The Gold Placers of Parts of Seward Peninsula, Alaska, including the Nome, Council, Kougarok, Port Clarence, and Goodhope Precincts; by Arthur J. Collier, Frank L. Hess, Philip S. Smith, and Alfred H. Brooks. Pp. 343, with 11 plates and 19 figures.

No. 329. Organization, Equipment, and Operation of the Structural-Materials Testing Laboratories at St. Louis, Mo.; by Richard L. Humphrey, with preface by Joseph A. Holmes. Pp. vi, 84, with 25 plates and 9 figures.

No. 330. The Data of Geochemistry; by Frank Wigglesworth Clarke. Pp. 716. See vol. xxv, p. 458.

No. 331. Portland Cement Mortars and their Constituent Materials. Results of Tests made at the Structural-Materials Testing Laboratories, Forest Park, St. Louis, Mo., 1905–1907; by Richard L. Humphrey and William Jordan, Jr. Pp. vii, 130, with 20 plates and 22 figures.

No. 332. Report of the U. S. Fuel-Testing Plant, at St. Louis, Mo. January 1, 1906, to June 30, 1907. Joseph A. Holmes in charge. Pp. 1–299.

No. 333. Coal-Mine Accidents; Their Causes and Prevention. A preliminary statistical Report; by Clarence Hall and Walter O. Snelling, with introduction by Joseph A. Holmes. Pp. 21.

No. 334. The Burning of Coal without Smoke in the Boiler Plants: a Preliminary Report; by D. T. Randall. Pp. 26, with 3 tables.

No. 336. Washing and Coking Tests of Coal and Cupola Tests of Coke, conducted by the U. S. Fuel-Testing Plant at St. Louis, Mo. January 1, 1905, to June 30, 1907; by Richard Molenke, A. W. Belden and G. R. Delamater, with introduction by J. A. Holmes. Pp. 1–76.

No. 339. The Purchase of Coal under Government and Commercial Specifications on the Basis of its Heating Value: with Analyses of Coal delivered under Government Contracts; by D. T. RANDALL. Pp. 27.

No. 343. Binders for Coal Briquets. Investigations made at the Fuel-testing Plant, St. Louis, Mo.; by JAMES E. MILLS. Pp. 56 with 1 figure.

WATER-SUPPLY AND IRRIGATION PAPERS.—No. 212. Surface Water Supply of the Great Basin Drainage 1906; by E. C. LA RUE, THOMAS GRIEVE, JR., and HENRY THURTELL. Pp. iv, 98, with 2 plates and 2 figures.

No. 213. The Surface Water Supply of California, 1906. With a Section on Ground Water Levels in Southern California. (Great Basin and Pacific Ocean Drainages in California and Lower Colorado River Drainages); by W. B. CLAPP. Pp. 219, with 4 plates and 2 figures.

No. 214. Surface Water Supply of the North Pacific Coast Drainage, 1906; by J. C. STEVENS, ROBERT FOLLANSBEE, and E. C. LA RUE. Pp. vi, 208, with 3 plates and 2 figures.

No. 215. Geology and Water Resources of a Portion of the Missouri River Valley in Northeastern Nebraska; by G. E. CONDRA. Pp. 59 with 11 plates.

No. 217. Water Resources of Beaver Valley, Utah; by WILLIS T. LEE. Pp. 57, with 1 plate and 3 figures.

3. *Maryland Geological Survey;* WILLIAM BULLOCK CLARK, State Geologist. Volume VI, pp. 572, pls. 51, figs. 19, with map. Baltimore, 1906.—Part I of the present report on the physical features of Maryland, by William Bullock Clark and Edwin B. Mathews, is a somewhat elaborate compendium of the geological and geographical features of the state, including the physiography, geology, mineral resources, soils, climate, forestry, etc. The report on the highways of Maryland, by A. N. Johnson, and state highway construction, by Walter Wilson Crosby, make up Parts III and IV, while Part V is a history of the origin, boundaries, etc., of the counties of Maryland. A new geological and soil map accompanies these descriptions. A large part of the material contained in this volume has been previously published as descriptive matter relating to Maryland's exhibit at the Louisiana Purchase Exposition and in its present form will reach a greater number of readers. H. E. G.

4. *Iowa Geological Survey,* SAMUEL CALVIN, State Geologist, JAMES H. LEES, Assistant State Geologist. Volume XVII; *Annual Report for 1906, with Accompanying Papers.* Pp. 588, pls. 62, figs. 44. Des Moines, 1907.—The report for 1906 deals largely with the economic resources of the state and includes a study of Portland cement and the geology of quarry products in general. There are included analyses of coals, limestones, chalks, clays, shales, and marls and an account of tests of the Iowa building stone.

A new geological map of the state, compiled by T. E. Savage, accompanies this report. H. E. G.

5. *Wisconsin Geological and Natural History Survey,* E. A. Birge, Director.—The Wisconsin Survey has recently issued four road pamphlets, of 24 to 54 pages each, by the Highway Engineer, A. R. Hirst. The topics discussed are : Earth roads, Stone and Gravel Roads, the Earth Road drag, and Culverts and Bridges.

6. *Geological Map of Cape of Good Hope.*—Four new sheets of the Geological Map, by A. W. Rogers and A. L. Du Toit, have been issued. No. 42 covers the region between Kimberley and Hopetown, and No. 52 an area from Mafeking westward to longitude 24° and from the Molopo river southward to latitude 26° 30′. No. 49 is the Kuruman and No. 50 the Vryburg sheet. H. E. G.

7. *Variations Périodiques des Glaciers, XIIme Rapport, 1906 ;* par Dr. Ed. Bruckner et E. Muret. Extrait des Annales de Glaciologie ii, March, 1908, pp. 161–198. (Frères Borntraeger Éditeurs). Berlin, 1908. Also *Zeitschrift für Gletscherkunde ;* Band II, Heft 3, pp. 161–234. Berlin, 1908.—The report on glaciers for 1906 presents facts similar to those of the last five years. In the eastern Alps, of twenty-six glaciers reported three remained stationary and one was advancing. The Italian glaciers are all in retreat, and in Savoy and in the Pyrenees many small glaciers and even certain névé fields have disappeared. In the Bukhara mountains one glacier in the Pierre le Grand chain has a marked advance. In the glaciers of North America there has been a decided shrinkage, with the exception of the remarkable glacier in Yakutat Bay, described by Tarr. H. E. G.

8. *The Ceratopsia ;* by John B. Hatcher, based on preliminary studies by Othniel C. Marsh. Edited and completed by Richard S. Lull. Monograph XLIX, U. S. Geological Survey, pp. 198, pls. 51, and 125 figures in the text. Washington, 1898.—This volume constitutes the third of six extensive monographs planned by the late Professor O. C. Marsh on the extinct vertebrates of North America. One, on the Odontornithes, or toothed birds, was published in 1880 ; a second on huge horned mammals, the Dinocerata, in 1884, while the present volume on the horned dinosaurs has just appeared. The remaining three are in course of preparation.

Under Professor Marsh's direction, many of the illustrations for these volumes were made both lithographic and on wood, and a series of preliminary notices, largely descriptions of new species, were published from time to time in this Journal. In the present instance, the notices were 16 in number, the lithographic plates 19, while of the woodcuts there were 28.

After Professor Marsh's death, in 1899, Professor H. F. Osborn, who succeeded the former as Vertebrate Paleontologist to the U. S. Geological Survey, assigned the Ceratopsia volume to Mr. J. B. Hatcher, the discoverer and chief collector of this remarkable group of reptiles. Hatcher in turn carried the work forward, adding many of the remaining text-figures and plates as well as 157 printed pages of the text. After having completed the morphology and specific descriptions, Mr. Hatcher died on July 3, 1904, and it became necessary for a third author to pick up the threads of the task and carry the work to completion. This has been done by Professor Richard S. Lull, of Yale University, who has edited the whole volume and, in addition, added the final section including the generic and specific summary; the geology and physiography of the Ceratopsia localities and the discussion of the evolution, probable appearance, habits and causes of extinction of the race.

The book includes an extensive biographical notice of Mr. Hatcher by Professor Osborn, who expresses the hope that the volume may prove to be a lasting monument to the rare and noble spirit of John Bell Hatcher.

III. Miscellaneous Scientific Intelligence.

1. *Harvard College Observatory*, Edward C. Pickering, Director.—Recent publications from the Harvard Observatory are noted in the following list (continued from vol. xxv, p. 460):

Annals.—Vol. XLIX, Pt. II. Peruvian Meteorology; by Solon I. Bailey. Observations made at the Auxiliary Stations 1892–1895. Pp. 107–232 with 80 tables and 2 figures.

Vol. L. Revised Harvard Photometry. A Catalogue of the Positions, Photometric Magnitudes and Spectra of 9110 Stars, mainly of the magnitude 6·50, and brighter. Observed with the 2 and 4 inch meridian photometers. Pp. iv, 252, with 4 tables.

Vol. LXI, Pt. I. Researches of the Boyden Department; by William H. Pickering. Pp. vi, 103, with 3 plates.

Circular No. 136. Comparison Stars for U Geminorum. Pp. 3.

2. *Publications of the Allegheny Observatory of the Western University of Pennsylvania.*

Vol. I, No. 3. The Orbit of α Andromedæ. By Robert H. Baker. Pp. 17–24.

Vol. I, No. 5. The Orbit of Algol from Observations made in 1906 and 1907. By Frank Schlesinger and R. H. Curtiss. Pp. 25–33.

3. *Carnegie Institution of Washington.*—Recent publications of the Carnegie Institution are given in the following list (continued from vol. xxv, p. 163):

No. 66. High Steam Pressures in Locomotive Service; by William F. M. Goss. Pp. 144.

No. 82. The Physiology of Stomata; by Francis E. Lloyd. Pp. 142, with 14 plates and 40 figures.

No. 85. Index of Economic Material in Documents of the States of the United States. New York 1789–1904. Prepared for the Department of Economics and Sociology of the Carnegie Institution of Washington; by Adelaide R. Hasse. Pp. 553.

Also the same for Rhode Island; by Adelaide R. Hasse. Pp. 95.

No. 92. Guide to the Archives of the Government of the United States in Washington; by Claude H. Van Tyne and Waldo G. Leland. Second Edition, revised and enlarged, by

W. G. Leland. (Revised edition of Publication No. 14.) Pp. xiii, 327.

4. *Maryland Weather Service;* Wm. B. Clark, Director. Volume II, pp. 515, with 169 figures and 24 plates. Baltimore, 1907.—The first volume of the Maryland Weather Service, issued in 1899 (see vol. ix, 234), contained a general account of the physiography and meteorology of the state. In the present work the climatic features of the city of Baltimore are made the subject of detailed study, this being based upon a series of observations extending over a period of nearly a century. The systematic thoroughness and minuteness with which Dr. O. L. Fassig has gone into this subject, and the fulness with which the various topics are illustrated by tables, figures and charts, makes the volume, as a whole, almost unique in meteorological literature, and gives it much more than a local interest. The introduction (pp. 21–26), on the operations of the service, has been prepared by the Director.

5. *The Apodous Holothurians. A Monograph of the Synaptidæ and Molpadiidæ;* by Hubert Lyman Clark. Smithsonian Contr. to Knowledge, vol. xxxv, 231 pages; 13 plates.—This is a very much needed and useful work on a group of holothurians that is comparatively little known. All the genera and species are described, the original descriptions and figures being copied when authentic specimens were not available. The anatomy and histology are given pretty fully in many cases. It includes many new species, mostly from the deep seas, and some new genera, as well as new limitations of old ones. There is a full biblography and index. A. E. V.

6. *American Association for the Advancement of Science.*—The summer meeting of the American Association will be held at Hanover, N. H., from June 29 to July 4. The American Physical Society will meet in conjunction with Section B. Various interesting excursions, to the White Mountains and elsewhere, have been arranged.

7. *International Catalogue of Periodicals.*—Professor E. Guarini has recently issued a catalogue of 4063 periodicals classified by country and subject. MM. Dunod and Pinat, Paris, are the publishers.

Obituary.

M. Albert Lapparent, the eminent French geologist, died in May last at the age of sixty-seven years.

Professor Karl August Möbius, Director of the Zoological Museum at Berlin, died on April 26 at the age of eighty-three years.

M. Pierre J. A. Béchamp, the veteran French chemist, died on April 15 at the age of ninety-two years.

Dr. Robert Chalmers, of the Canadian Geological Survey, died on April 9 at the age of seventy-four years.

William A. Anthony, Professor emeritus of physics, electrical and mechanical engineering at Cooper Union, New York City, died on May 29 at the age of seventy-three years.

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SCIENTIFIC INTELLIGENCE.

Librarian U. S. Nat. Museum.

VOL. XXVI. AUGUST, 1908.

Established by BENJAMIN SILLIMAN in 1818.

THE AMERICAN JOURNAL OF SCIENCE.

EDITOR: EDWARD S. DANA.

FOURTH SERIES

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THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

Art. XII.—*The Rôle of Water in Tremolite and Certain Other Minerals;* by E. T. Allen and J. K. Clement.

Object of the Investigation.—A study of the composition of tremolite was undertaken with several objects in view. In the first place, it belongs to the series of calcium and magnesium metasilicates, all the other known members of which have already been studied in this laboratory. Secondly, it is the simplest known amphibole with the exception of kupfferite, and consequently affords an advantageous opportunity for further study of the relations which exist between the amphiboles and the pyroxenes. For a complete investigation of this kind, pure minerals are necessary, and since natural minerals can rarely be classed as such, we sought to prepare tremolite synthetically. But, the ordinary methods proving inadequate to the task, we proceeded to a study of the natural mineral, in order that we might find out what elements were really essential to it, as well as what physical conditions were necessary to its existence.

One of the most important questions which presented itself in this connection was whether the mineral must be synthesized by wet or dry methods; whether it was hydrous or anhydrous. Some preliminary work which we had done proved that it was incapable of existence above about 1000°–1100°, a temperature at which it is still in the solid state. Attempts to form it by heating a glass of the same composition below this temperature, or by rapid cooling of the melt, failed, indicating not only that the natural mineral must have been formed from solution, a conclusion in accord with geological evidence, but further, that it could be obtained in no other way. At first, molten salts were tried as solvents, on account of the difficulty of working with water at temperatures much above the ordinary. These efforts also proving unsuccessful, the idea suggested itself that the mineral was perhaps hydrous and therefore must be made by the agency of water, in spite of the general opinion among mineralogists that tremolite is anhydrous.

Material for Study.—In order to establish the true composition of tremolite, we made a careful selection of specimens from five different sources. The color of the specimens indicated that they contained very little iron and the microscopic examination showed them quite free from inclusions, though some of them required separation from comparatively coarse grains of other minerals intergrown with or adhering to them. This was done with heavy solutions, either potassium mercuric iodide, or mixtures of methylene iodide and benzene. After it had been ascertained by the microscope that each specimen was as pure as it was practicable to get it, it was carefully analyzed. The results are given in Table I. An inspection of the five analyses (I-V) shows that water* is present in all of them and ranges from 1·72–2·50 per cent, averaging 2·17 per cent in the two purest specimens. It may therefore be regarded as

TABLE I.—ANALYSES OF NATURAL TREMOLITES.

	Localities						
	1 Ham Island, Alaska	2 Ossining, N. Y.	3 Gouverneur, N. Y.	4 Russell, N. Y.	5 Edwards, N. Y.	6† Richville, N. Y.	7† Lee, Mass.
SiO_2	58·59	57·35	56·92	56·36	58·24	57·45	57 69
TiO_2	--	·07	·10	·06	·04	--	·14
Al_2O_3	·10	1·21	1·65	1·88	·60	1·30	1·80
Fe_2O_3	--	·11	·36	·61	·43	·18	none
FeO	--	·23	none	1·01	none	·22	·55
MnO	--	·01	--	·04	1·28	·07	trace
MgO	24·78	23·87	23·81	22·97	25·16	24·85	24·12
CaO	13·95	14·02	12·51	12·82	10·85	12·89	13·19
Na_2O	·12	·42	1·22	·94	82	·67	·48
K_2O	·10	·19	·60	·74	·19	·54	·22
H_2O	*2·31*	*2·21*	*2·01*	*1·72*	*2·50*	*1·25*	*1·66*
F	none	·11	1·03	1·23	·24	·77	·37
	99·95	99·80	100·21	100·38	100·35	100·19	100·22
O equivalent to F	·00	·05	·43	·53	·10	·32	·15
	99·95	99·75	99·78	99·85	100·25	99·87	100·07

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* The water was determined by absorption by calcium chloride. See Hillebrand, Analysis of Silicate and Carbonate Rocks, Bull. U. S. Geol. Surv., 305, p. 62.

† Analyses 6 and 7 were made by Penfield and Stanley.

an essential constituent. While work on this subject was in progress, Penfield and Stanley[*] published the analyses of a number of amphiboles, including two tremolites, all made on very carefully selected material, in which it was found that all contained notable quantities of water and fluorine. While our results confirm theirs in regard to water, it may be noted in passing that fluorine is entirely absent from one of our specimens and occurs in quite insignificant quantities in one or two others. It is not, therefore, to be counted an essential constituent.

The rôle of the water.—The next question to present itself is: What part does the water play in the constitution of the mineral? Is it chemically combined or dissolved, i. e., does it escape at one or more temperature points with a sudden change in physical properties, or is it given off gradually through a range of temperatures, the physical properties varying with the change in composition?

Tammann,[†] in attacking a similar problem with the zeolites, used the method originated by Van Bemmelen. The powdered minerals, in small beakers, were left to stand, at constant temperature (19°), in desiccators with sulphuric acid of various concentrations, the vapor pressures of which were known, until the weight became constant. This method had the disadvantage of removing only a fraction of the total water, 1·1 per cent to 23 per cent, according to the mineral, leaving one still in doubt about the major part of the water. This difficulty is obviated by the more direct method of Friedel,[‡] who heated the zeolites, at progressively higher temperatures, in a current of air which was saturated with water at an approximately constant temperature, this temperature remaining nearly the same in all the experiments of any one series. He found thus for several zeolites true equilibria at every temperature.

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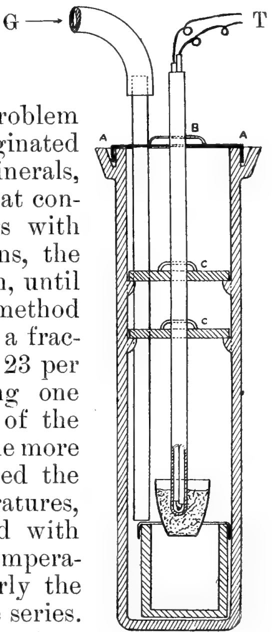

G=Air current, T=thermoelement.

The Apparatus.—Some preliminary experiments on tremolite suggested that the vapor pressure, even at higher temperatures, would probably fall practically to zero within a limited time. We therefore adopted Friedel's method,

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[*] This Journal (4), xxiii, p. 23, 1907.

[†] Zeitschr. Phys. Chem., xxvii, 323, 1898.

[‡] Bull. Soc. Min., xix, 363, 1896; xxii, 5 and 86, 1899.

only heating in a current of *dry* instead of *moist* air.* The air was dried by concentrated sulphuric acid. The apparatus in which the dehydration was carried on is shown in fig. 1. It is a cylinder of Berlin porcelain, closed at one end and glazed on the inside to make it impervious to gases. The upper end is molded so as to form a groove, into which fits the iron cover. There are also two inner covers of porcelain, each 1^{cm} thick, which rest on lugs baked on to the inner wall of the cylinder. These keep the temperature more nearly constant and protect the iron cover from excessive heat. All three covers are perforated near the edge to allow the passage of two porcelain tubes. One of these, which is closed at the bottom, reaches down to the charge and carries the thermo-element. The other is open at both ends, reaches nearly to the bottom of the cylinder, and admits the current of dry air. One of the tubes may be fitted closely to the iron cover by a "fibre" ring, the other may be left loose enough to allow the escape of the air. If it is desired to use some other atmosphere in the furnace, mercury may be poured into the groove to more effectually prevent any air from leaking in. The crucible which holds the tremolite rests on a platinum triangle which is supported by a hollow cylinder of fine white clay. This whole apparatus in an upright position is then slipped into a platinum resistance coil furnace which envelopes it to within 2^{cm} of the top. The furnace is heated by a storage battery and the temperature can be regulated very closely indeed for a period of many hours.

Conditions of Experiment.—There was no difficulty in maintaining the temperature within 5° without much attention, except when the same battery was required intermittently for other work. In such cases there were sometimes aberrations of 10° or more. As the time of experiment is not essential, a fall in temperature is of no importance; a half hour or more at a temperature as much as 5° below the point aimed at was not counted. On the other hand, if the temperature ran 5° or more above the point, the work was rejected unless the charge underwent further loss at the same temperature on the following day. The loss of water was so very slow that an aberration of this kind scarcely ever affected the results. Besides, our object was only to determine the form of the curve with sufficient accuracy to settle the question whether the loss of water was continuous or discontinuous.

Regarding the conduct of an experiment only a few words of explanation are needed. The mineral was generally in the form of a rather coarse powder, ground only fine enough to pass a screen of 100–120 meshes to the linear inch, because

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* The question of equilibrium is raised on p. 117.

fine powders are known to absorb moisture from the air.* The crucible containing the powder was introduced into the furnace, rapidly heated to the required temperature and kept there during the rest of the working day. Then it was quickly transferred to a sulphuric acid desiccator, cooled and weighed. The time of cooling was usually about 20 minutes. There is some chance of error here, in that the mineral may have absorbed moisture or air during the cooling. Friedel† found that a nearly dehydrated chabazite absorbed 2·34 per cent of air when left in a desiccator several hours. Such errors must be small in tremolite, for the time of cooling seemed to make no difference in the apparent weight and the substance did not show a tendency to gain on the balance except after heating at the lower temperatures where the losses were small.

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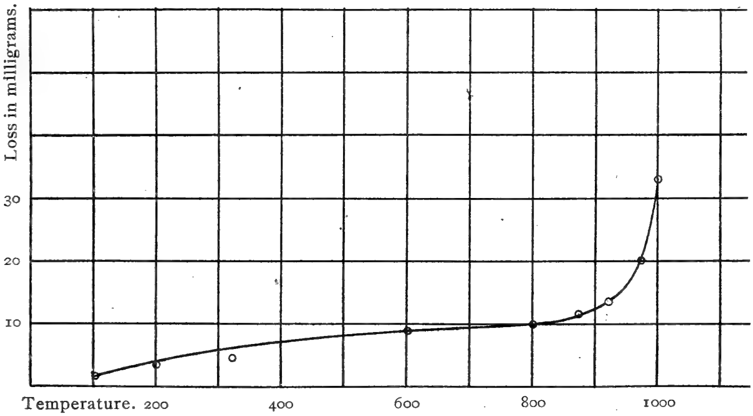

Curve showing loss of water in tremolite from Gouverneur, N. Y. The losses are too small but the form of the curve will be seen to resemble closely those in fig. 3, where the work was more exact.

The heating at each temperature was continued until practically constant weight, i. e., until the loss in 5–6 hours was not more than 1–3 tenths of a milligram.

Curves showing loss of water with temperature.—The first work was done on the tremolite from Gouverneur, N. Y. The results are plotted in fig. 2. It was afterwards found that the work was quite imperfect because, instead of heating to a constant weight, what was considered an ample period of time

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* Day and Allen, this Journal, xix, 127, 1905. Mauselius, Arsbok Sveriges Geologiska Undersökning No. 3, 1907. W. F. Hillebrand, private communication. Much more complete treatment in paper about to be published.

† Bull. Soc. Min., xxii, p. 15, 1899; see also Hillebrand, loc. cit., p. 50.

was allowed for complete dehydration. The losses are therefore too small, but since the general form of the curve is similar to that of the others, and the *form* of the curve is the most important point, the curve is given for the sake of completeness. The curve for the tremolite from Ham Island, Alaska, the purest of all the specimens, was determined with the greatest degree of completeness. On account of the tedious nature of the work,* fewer points were determined on the other curves, and in none of them was the dehydration carried to the end, but only so far as to show beyond doubt that all the curves were of the same general form. An exception should be made of the specimen from Russell, N. Y. (IV–IV, fig. 3), which contains less water and more iron than any of the rest. There is an interruption in the continuity of the curve between 835° and 865° where no water appeared to be given off. A partial explanation may be found in the fact that oxygen appears to be absorbed here; at any rate the powder, at first slightly greenish, becomes brown on continued heating. This absorption might partly offset the loss of the water. The data from which all the curves are plotted are found in Tables 2, 3 and 4.

Table II.—Loss of Water by Heat. Tremolite (Ham Island, Alaska).
2 grams powdered mineral taken.

	Time	Temperature	Weight	Loss
	0 hrs.	----	26·6865	·00
1	5¾ “	500°	26·6798	·0067
2	5 “	500°	26·6798	·0067
1	5 “	750°	26·6781	·0084
2	5½ “	750°	26·6780	·0085
1	5 “	801°	26·6781	·0084
2	4½ “	805°	26·6778	·0087
1	5 “	845–850°	26·6774	·0091
2	6 “	845°	26·6776	·0089
1	4 “	863°	26·6772	·0093
2	6 “	863°	26·6769	·0096
3	5 “	863°	26·6764	·0101
4	5 “	860°	26·6761	·0104
5	6 “	862°	26·6763	·0102
1	4½ “	877°	26·6758	·0107
2	2½ “	875°	26·6756	·0109
1	2½ hrs.	890°	26·6753	·0112
2	3 “	890°	26·6751	·0114
3	5 “	894°	26·6744	·0121
4	4½ “	890°	26·6743	·0122
1	2 “	920°	26·6739	·0126
2	6 “	918°	26·6722	·0143
3	7 “	918°	26 6721	·0144
1	6 “	933°	26·6701	·0164
2	6 “	933°	26·6680	·0185
3	6 “	933°	26·6667	·0198
4	6 “	930°	26·6658	·0207
5	5 “	933°	26·6646	·0219
6	3 “	930°	26·6644	·0221

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* If any fluorine escaped during the dehydration of the other tremolites, it must have been very little, for the microscope did not detect any lack of homogeneity, while, when the Gouverneur tremolite was heated 240 consecutive hours at about 950°, the loss was 0·5 per cent in excess of the water and the mineral showed a very evident change.

TABLE III.—TOTAL LOSS AT DIFFERENT TEMPERATURES. TREMOLITE (Ham Island, Alaska).

Grams taken	Time	Temperature	Loss	Proportional loss for 2 gr.	Percentage loss	Per cent of total water
2	10¾ hrs.	500°	6·7 mg.		·33	14·5
	10½ “	750°	8·5 “		·42	18·3
	9½ “	805°	8·7 “		·43	18·8
	11 “	845–850°	9·1 “		·45	19·6
	26 “	863°	10·4 “		·52	22·5
	7 “	875°	10·9 “		·54	23·4
	15 “	890°	12·2 “		·61	26·3
	15 “	918–920°	14·4 “		·72	31·1
	32 “	930–933°	22·1 “		1·10	47·7
5	8½ “	200°	10·9 “	4·4	·22	9·5
	8½ “	300°	13·0 “	5·2	·26	11·2
	10 “	400°	15·5 “	6·2	·31	13·4
	12½ “	500°	17·3 “	6·9	·35	14·9
	13½ “	600°	20·4 “	8·2	·41	17·7
	7½ “	725°	21·8 “	8·7	·43	18·8
	5½ “	800°	22·5 “	9·0	·45	19·4
	10 “	915°	34·2 “	13·7	·68	29·6
about	100 “	960°	115·8 “	46·3	2·31	100·0

Interpretation of the curves.—It will be seen that all the curves (fig. 3) rise very slowly and in nearly a straight line until a point approximating 850° is reached, when they bend strongly upward. The point seems to vary somewhat with the composition of the mineral. The curves appear to be smooth; still one might suspect that so strong a change in curvature indicated some abrupt change in the physical or chemical condition of the mineral. The microscopic evidence shows, however, that the crystal form, with such optical properties as can be quantitatively measured—extinction angle, index of refraction—remain almost unchanged. In the purer specimens from Ham Island and Ossining, and in that from Gouverneur, there is no essential difference between the mineral before and after heating, except in the development of bubbles throughout the mass, which increase in number as more water is lost. In the Edwards specimen, a beautiful parting parallel to the base continued exactly as it was before heating. There is a change in the color of the specimen from pink to dull greenish, which is probably due to the absorption of oxygen by the manganese oxide, 1·28 per cent of which is present. This, however, has nothing to do with the bend in the curve, for the color change was just as noticeable in a portion of the mineral which had been heated below 850°. The water in all the specimens is lost gradually as the temperature rises without any sudden change of properties or loss of homogeneity.* It cannot, therefore, be chemically combined, even though it is

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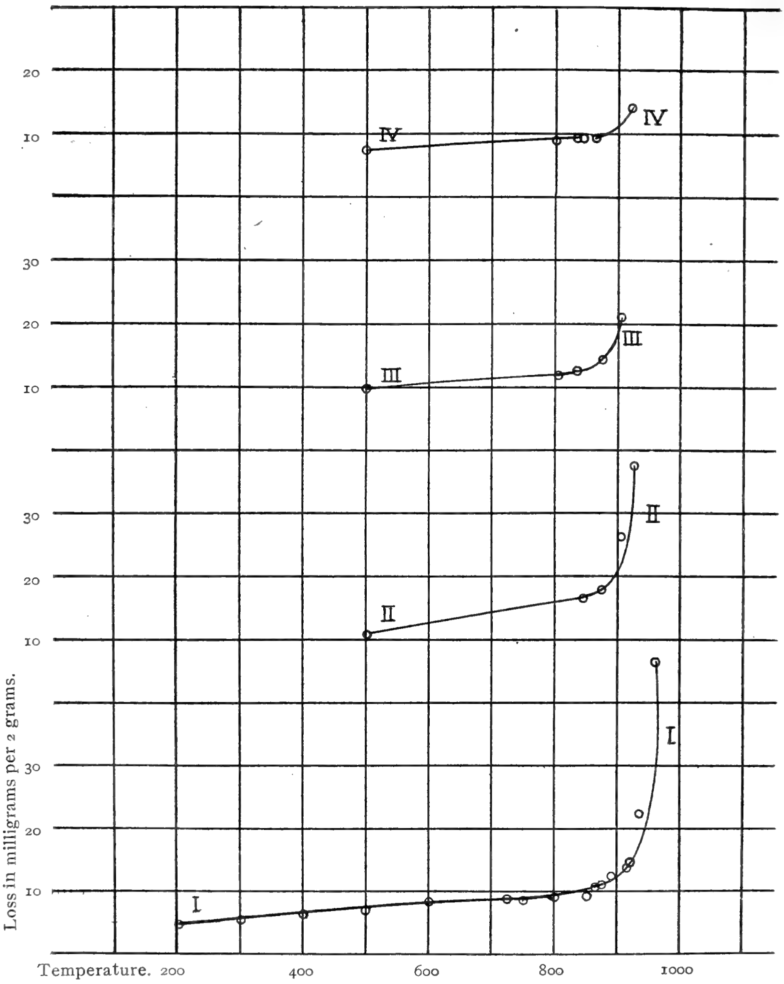

I. Tremolite from Ham Island, Alaska.
II. " " Ossining, N. Y.
III. " " Edwards, N. Y.
IV. " " Russell, N. Y.

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* Making the above-mentioned reservation regarding the specimen from Russell, N. Y.

TABLE IV.—TOTAL LOSSES OF WATER AT DIFFERENT TEMPERATURES.

Tremolite from	Time	Temperature	Loss mg.	Per cent loss	Per cent of total water
Ossining, N. Y.	11½ hrs.	500°	10·9	·54	24·7
2 gr. taken	14½ "	840–5°	16·5	·82	33·3
	29½ "	870–5°	17·9	·89	39·4
	67½ "	904°	26·2	1·31	59·2
	95¾ "	923°	37·6	1·88	85·1
Gouverneur, N. Y.		100°	1·7		
2 gr. taken		200°	3·3		
		320°	4·5		
		608°	7·7		
		805°	9·8		
		880°	11·1		
		920°	13·7		
		980°	20·1		
Russell, N. Y.	12 hrs.	500°	7·7	·38	22·4
2 gr. taken	10 "	800°	9·0	·45	26·2
	8 "	835°	9·4	·47	27·3
	4 "	845°	9·4	·47	27·3
	4 "	865°	9·4	·47	27·3
	10 "	920°	14·2	·71	41·4
Edwards, N. Y.	11 "	500°	9·9	·50	19·8
2 gr. taken	15½ "	800–5°	11·9	·59	23·8
	15½ "	835°	12·4	·62	24·8
	33 "	875°	14·4	·72	28·8
	37½ "	905°	21·2	1·06	42·4

given off so very slowly at a temperature of 900°. That it is mechanically held seems entirely improbable, for there is no indication of a spongy structure to be found by microscopic analysis. If capillary pores exist they are submicroscopic. The phenomenon is in all probability molecular; the water is therefore to be regarded as *dissolved*, and the mineral as a solid solution. Mineralogists and chemists are wont to regard the retention of water at a high temperature as proof of chemical combination, but all ideas agree that a true hydrous compound cannot lose water without becoming inhomogeneous. The behavior of tremolite is comparable with that of the zeolites in the two essential points above mentioned. In the latter, however, the quantity of water is very much greater, and presumably for this reason the change in birefringence and volume which they undergo when dehydrated is much more noticeable. In the zeolites, as in tremolite, dehydration is very slow and requires in some cases a temperature of 500° for its completion.

Friedel's data for chabazite, analcite and mesolite are plotted in figs. 4 and 5. The similarity in the form of the curve of mesolite to that of tremolite will be seen at once. Friedel did not class the zeolites with solid solutions, but Tammann did so, and as such they are now generally regarded. They have remained as a unique class of minerals. The behavior of tremolite now shows that the zeolites are not the only ones which

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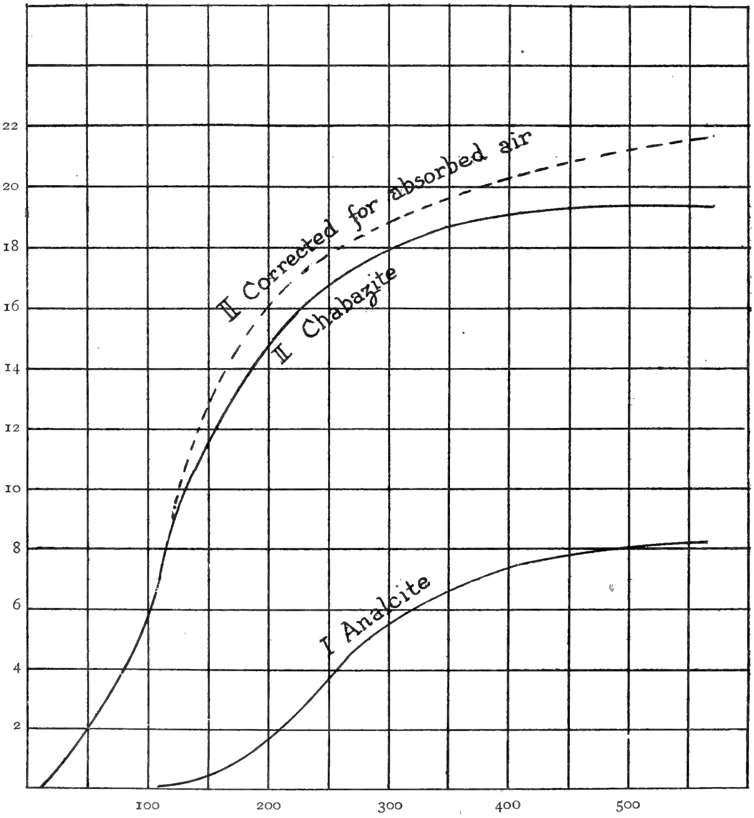

Curves showing loss of water from analcite (I) and chabazite (II) at different temperatures. Plotted from Friedel's data. Bull. Soc. Min., xix, p. 376, 1896 ; xxii, p. 14, 1899.

contain dissolved water, and it occurred to us that the class might not be uncommon.

Dissolved water in other minerals.—From this standpoint, quartz, wollastonite, garnet, adularia, kupfferite, diopside and beryl were studied. They were coarsely powdered to avoid condensation of moisture from the atmosphere, and then heated. Water-clear quartz from Middleville, Herkimer County, N. Y., ground to 40 mesh and dried thoroughly at 110°, lost only 0·10 per cent of its weight on blasting. Transparent crystals of adularia from St. Gothard, Switzerland, treated in the same way, lost 0·12 per cent; wollastonite from Natural Bridge, N. Y., lost 0·27 per cent, and lime garnet from Piedmont, Italy, lost 0·26 per cent. These losses are too small to be of much interest in this connection, but the remaining minerals, kupfferite, diopside and beryl, were found to contain much larger quantities.

Kupfferite.—The specimen examined was from Edwards, N. Y., where it occurs intergrown with the tremolite, from which it was separated by heavy solutions. It is prismatic and fibrous, straw-colored or white, has an index of refraction $\gamma = 1{\cdot}62$, and shows parallel extinction. A portion was analyzed and the results are appended. The amount of this was small and the portion which was experimented on was obtained afterwards and was somewhat purer.

	Analysis
SiO_2	59·29
TiO_2	·03
Al_2O_3	·59
Fe_2O_3	·29
FeO	·06
MnO	2·77
MgO	30·98
CaO	1·26
Na_2O	·37
K_2O	·19
F	·20
H_2O	3·80
	99·83
O equivalent to F	·08
	99·75

	Calculated for $MgSiO_3$ which kupfferite approaches
SiO_2	60 per cent
MgO	40 "

Heated in dry air, the mineral behaved as follows:

TABLE V.

Charge, 2 grams

Time of heating	Temperature	Total loss in mg.	Loss per day in mg.
6 hours	400	5·9	5·9
3½ "	"	5·2	— ·7
6½ "	"	5·8	+ ·6

TABLE V (continued).

Charge, 2 grams

Time of heating	Temperature	Total loss in mg.	Loss per day in mg.
4½ hours	600	6·5	·7
6 "	"	7·2	·7
6 "	"	8·0	·8
6½ "	"	9·0	1·0
5½ "	"	9·4	·4
6 "	"	9·9	·5
6½ "	"	10·5	·6
6½ "	"	10·9	·4
6½ "	"	11·3	·4
6½ "	"	12·0	·7

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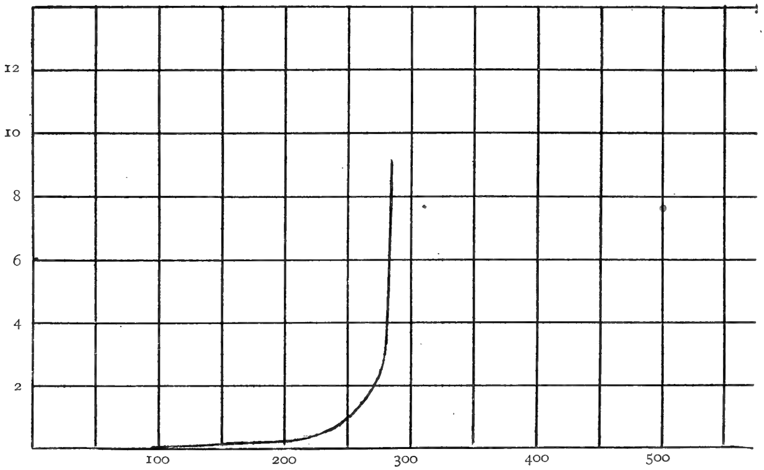

Curve showing loss of water from mesolite at different temperatures. Plotted from Friedel's data. Bull. Soc. Min., xxii, pl. opposite p. 89, 1899.

After about 60 hours' heating at 600°, the mineral had therefore lost $\frac{\cdot 012}{2\cdot 0} = 0\cdot 6$ per cent of water and was still losing at about the same rate, viz., about $\cdot 5^{mg}$ per day. An estimation of the vapor pressure of the water over the mineral was made by measuring the rate of flow of the air through the furnace, taking into account the water which escaped during the same time. During a day of six hours, this amounted to 1570^{cc}, while the average loss of water was about $\cdot 5^{mg}$, which, under these conditions, would occupy a volume of approximately 1^{cc}. The partial pressure of the water vapor would therefore be about 1/1500 of an atmosphere or about 0·5^{mm} of mercury. As it appeared that the loss of water under these conditions goes on indefinitely, a new series of experiments was made in which the mineral was heated in air which had been bubbled through 65 per cent (by weight) sulphuric acid having a vapor pressure at 25°, about the room temperature, of 3^{mm}. The results follow:

TABLE VI.

Time of heating	Temperature	Total loss in mg.	Loss per day in mg.
6 hours	600°	12·8	·8
4½ "	"	12·5	— ·3
6½ "	"	13·3	·8
7 "	"	13·7	·4

It will be seen that the average loss is practically the same as before. At this point, a small portion of material was removed from the crucible and examined microscopically. No essential change had taken place in its optical properties.

The remainder was now ground fine enough to pass a screen containing 150 meshes to the linear inch, and a new charge of 1·6428 grams was taken. This was heated at 820° in an atmosphere saturated with water vapor, which at the temperature of the room should have a partial pressure of about 23^{mm}. The following are the results:

TABLE VII.

Time of heating	Temperature	Loss in mg.	Loss per day in mg.
5½ hours	820°	13·9	13·9
5½ "	"	17·5	3·6
6 "	"	18·4	0·9
6½ "	"	19·4	1·0
6½ "	"	19·6	0·2
6½ "	"	19·7	0·1

At this stage, the mineral having lost altogether 2·05 per cent of water, or 50 per cent of the total quantity, another portion was removed and examined microscopically. It still remained kupfferite, though a secondary change had taken place, due probably to the oxidation of the manganese. The color had become dull green, and dark brown patches, partially transparent, were visible on some crystals. This secondary change made further experiments useless. The material was probably absorbing oxygen, in which case the total loss would not represent all the water which escaped. The homogeneity of the substance is preserved then during the earlier stages of dehydration at least, though the experiments did not prove that the loss of water was continuous. If this were the case, however, and the water in kupfferite were dissolved, we can readily understand how, by the rapid cooling of a melt of the composition $MgSiO_3$,* there is formed an anhydrous substance having the properties of an amphibole and very closely resembling kupfferite in particular, though the latter contains nearly 4 per cent of water.

It has already been stated that the amphiboles analyzed by Penfield and Stanley all contained water. The following are their results:

Actinolite,	Greiner in Tyrol,	H_2O	= 1·81%
"	Russell, N. Y.,	"	= 1·60
"	Kragerö, Norway,	"	= 1·31
"	Pierrepont, N. Y.,	"	= 1·42
Hornblende,	Cornwallis, N. Y.,	"	= 1·30
"	Renfrew, Ont.,	"	= ·75
"	Ellenville, N. Y.,	"	= ·66

More recent results by Blasdale confirm these figures and include also glaucophane:†

Actinolite,	Berkeley, Cal.,	H_2O above 100	= 1·78%
"	San Pablo, Cal.,	" " "	= 2·58
Tremolite,	" "	" " "	= 2·25
Glaucophane,	" "	" " "	= 1·78
"	" "	" " "	= 2·57

A pargasite from Arroyo Hondo, Santa Clara County, Cal., recently analyzed by W. O. Clark, gave 3·16 per cent H_2O above 100°.‡

Two hornblendes analyzed by H. S. Washington gave results as follows:§

Hornblende from Linosa Island near Tunis contained ·19% H_2O
" " Kaersut, Greenland, " ·59% H_2O

A hornblende from Beverly, Mass., analyzed by F. E. Wright, contained 3·15 per cent H_2O.‖

These data are sufficient to show that tremolite, kupfferite, actinolite, glaucophane and pargasite all contain water ranging in quantity from 1·3 per cent to 3 per cent, most of which is retained at 110°. Hornblende also contains water, though usually in smaller quantity. In view of these facts it seems not unlikely that the water in all of them is not combined, but dissolved as it is in tremolite.

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* This Journal, xxii, 406, 1906. At the time of its discovery this was regarded by us as a true amphibole, since kupfferite was not then known to contain water.

† Contributions to the Mineralogy of California; Bull. Dep't of Geol., Univ. of Cal., vol. ii, No. 11, pp. 333, 334, 338–340.

‡ Paragenesis of Minerals in the Glaucophane-bearing rocks of California, J. P. Smith, Proc. Am. Phil. Soc., xlv, 237, 1906.

§ Private communication.

‖ Tschermak's Miner. Petrogr. Mittheil., xix, 312, 1900.

Diopside from Ham Island, Alaska.—This mineral was intergrown with the tremolite from the same locality, and like it was very pure. A specimen *finely ground* for analysis had the composition :

		Cal. for $CaSiO_3MgSiO_3$
SiO_2	54·65	55·6
Fe_2O_3	·13	---
CaO	25·27	25·9
MgO	18·78	18·5
K_2O	·07	---
Na_2O	·03	---
H_2O	1·45	---
	100·38	100·0

This material being exhausted, another hand specimen of the same lot was crushed to *40 mesh*, separated from a little tremolite and calcite by methylene iodide and benzene, and dried at 105°. On blasting it lost 1·01 per cent. The dehydrated mineral was entirely homogeneous and the optical properties remained almost unchanged. The formation of bubbles was evident, but they were less numerous than in tremolite. The curve of loss to 800° was as follows :

TABLE VIII.

Time	Charge, 3 grams Temperature	Total loss in mg.
10½ hours	400	3·7
39½ "	600	18·3
12 "	800	24·9

The water lost was thus 82 per cent of the total water.

Beryl from Alexander Co., N. C.—An analysis of this specimen was not made. The material for experiment was taken from a single transparent crystal which contained a little muscovite, but hardly more than traces. The beryl was crushed to 100 mesh because it was anticipated the dehydration would be slow and the smaller grains would facilitate its escape. The loss in weight on blasting was found to be 2·54 per cent. By absorption with calcium chloride, the water being liberated by fusion with soda, the quantity found was 2·67 per cent. The mineral after it had been blasted was microscopically examined and found to possess all the properties of beryl. The bubbles formed were numerous and conspicuous. After the mineral had been heated a comparatively short time at 400° it reached constant weight, the loss being 3·1^{mg}. At 800° the loss continued over a long period without showing any signs of ceasing. The results follow :

TABLE IX.

Charge, 2 grams

Time	Temperature	Total loss in mg.	Loss per day in mg.
6 hours	800	14·2	11·1
5½ "	"	18·0	3·8
6 "	"	21·4	3·4
6 "	"	23·8	2·4
4½ "	"	24·8	1·0
6½ "	"	26·2	1·4
6½ "	"	27·9	1·7
6 "	"	29·1	1·2
4 "	"	30·4	1·3
4 "	"	31·1	·7
6½ "	"	31·4	·3
7 "	"	32·2	·8
6½ "	"	33·0	·8
6 "	"	33·6	·6
6 "	"	34·3	·7
6 "	"	34·6	·3
6 "	"	34·9	·3
6½ "	"	35·4	·5
6½ "	"	36·3	·9
6 "	"	36·9	·6

The loss of water at 800° was so slow that it was suspected that in *dry* air it might be indefinite; in other words, that the vapor pressure never would fall to zero. It seemed worth while in this case to try another series of experiments in which the furnace was traversed by a current of air saturated with water at the room temperature,—about 25°. The case was like that of kupfferite, except that beryl undergoes no secondary change when heated in air to 800°, and work with it therefore seemed more promising. After continuing the dehydration for eight days, it was found that the loss during that time was almost identical with the loss in dry air during the same time.

TABLE X.

Time	Temperature	Total loss in mg.	Loss per day in mg.
6 hours	800°	15·4	15·4
7 "	"	19·3	3·9
5½ "	"	21·6	2·3
6 "	"	23·8	2·2
7 "	"	27·1	3·3
6½ "	"	27·6	·5
5½ "	"	29·5	1·9
6½ "	"	30·7	1·2

Total loss in 50 h. = 30·7$^{\text{mg}}$.

A reference to the previous table will show that the same weight of beryl lost in *dry* air during a period of nine days, or 51 hours, 30·4$^{\text{mg}}$. The tendency for the reaction to reverse itself, that is, for the mineral to absorb water, was tested in another way, viz., after the heating in moist air had been continued for 7 days, the loss then being $29{\cdot}5^{mg}$, the process was continued at 600° for one day. The gain was but $\cdot 10^{mg}$, or practically nothing. On the following day the heating was continued at 800°, when the loss was $1{\cdot}3^{mg}$, and finally on the next day the heating was again repeated at 600°. The gain was only $\cdot 2^{mg}$. Evidently, therefore, it is impossible to get equilibrium under such conditions as Friedel found he could do with certain zeolites.

The most obvious conclusion appears to be that the estimated vapor pressure, which is of the same order of magnitude with beryl as it is with kupfferite, is far too low and that it would require a long time for the maximum vapor pressure to develop, or perhaps the latter would finally reach a state of "false equilibrium."* This raises the question, whether or not the curves obtained for tremolite may not represent "false equilibria," but the tedious nature of the work at atmospheric pressure and the secondary importance of the question after the relation of the water to the other components had been established, decided us not to carry the matter further.

Resorption of water by tremolite when heated with water in a bomb to 400°.—Although no attempts were made to get true equilibrium between tremolite and water vapor, some efforts were made to find whether water was taken up by the dehydrated mineral under any conditions. The tremolite from Ossining, N. Y., which had been heated to a constant weight at 923°, where it lost 85·1 per cent of its water, was then soaked in water for 20 hours, dried at 110° and blasted. It was then found to contain 0·59 per cent of its weight, or 26·7 per cent of the original water content. It had therefore absorbed 11·8 per cent. A specimen of the Ham Island tremolite which had lost 47·7 per cent of its water at 933°, was heated in a bomb, with water at 400°, for 6 days. It was then dried at 110° and the water retained determined by blasting. It contained 2·15 per cent, while originally it held 2·31 per cent of water. There seems to be no difficulty, therefore, in reversing the process when the active mass of the water becomes sufficiently great. With beryl, however, the results were quite different. A portion of this mineral which had lost 1·52 per cent of its weight after a protracted heating at 800°, was heated with 15^{cc} water at 420° for four days. Then the beryl was removed and dried at 110°. On blasting 1·7568 gr. lost ·0203 gr.=1·15 per cent. The beryl originally contained 2·54 per cent water, so that the portion which was introduced into the bomb must have had $2{\cdot}54-1{\cdot}52=1{\cdot}02$ per cent. Hardly any water was therefore absorbed in the bomb.

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* Thermodynamics and Chemistry, Duhem. Translated by Burgess. Wiley & Sons, 1903, p. 369.

Summary.

1. A study of five different specimens of natural tremolite, two of them of exceptional purity, proves that all contain water ranging from 1·7 to 2·5 per cent. This water is lost gradually with rising temperatures without any loss in homogeneity and with very slight change in the optical properties. The water is therefore not chemically combined, although the mineral in the powdered state is not completely dehydrated under 900°. It is to be regarded as dissolved water, and tremolite as a solid solution. A diopside from a metamorphosed limestone contained 1 per cent of water and behaved in practically the same way, though presumably the diopside of eruptive rocks is anhydrous.

The amphibole kupfferite and a specimen of beryl contained respectively 3·8 per cent and 2·5 per cent of water, which they lost very slowly at comparatively high temperatures (400°–800°) and still retained their homogeneity. With them, however, the loss of water appeared to progress so slowly at these temperatures that the total water could not be driven off in any reasonable time. The beryl lost at the same rate for a long period, both in dry air and in an atmosphere containing water vapor at the partial pressure of about 23^{mm}, even though this rate appeared to show that the mineral possessed a vapor pressure of only about $0·5^{mm}$ of mercury. The kupfferite showed a similar behavior, but the fact that it suffered a secondary change in composition at the higher temperatures (probably due to the absorption of oxygen) made the experiments on it less satisfactory.

All these minerals show important points of resemblance with the zeolites, with which they may broadly be classed, but in one important particular they differ,—at least, this is true of kupfferite and beryl,—they do not give true equilibrium with water vapor at low pressures, while the zeolites under similar conditions do so (Friedel). Diopside and tremolite seem to give off their water continuously, but not indefinitely, with rising temperatures, though it is quite possible the curves represent cases of “false equilibria.”

2. Recent analyses indicate that all the amphiboles contain water. Actinolite, glaucophane, and pargasite contain 1·3–3 per cent, mostly retained above 100°. The hornblendes also contain water, though usually in smaller quantity. These facts, taken in connection with the above work on tremolite and kupfferite, lead to the suspicion that the amphiboles generally contain dissolved water as a characteristic constituent, and are solid solutions.

The authors wish to express their hearty thanks to Mr. F. E. Wright, to whom they are indebted for all the microscopic data found in this paper.

Geophysical Laboratory,
Carnegie Institution of Washington, April 23, 1908.

ART. XIII.—*A Quantitative Determination of the Radium Emanation in the Atmosphere;* by GEORGE C. ASHMAN.

IT was shown by Elster and Geitel[*] in 1902 that a negatively charged wire exposed for a few hours in the air receives a radio-active deposit similar in character to the quick-changing radium products. The first attempt to measure the amount of radio-active matter in the atmosphere was made by Eve[†] in 1905 in Montreal. The method used consisted in collecting the active deposit on a charged wire placed in a cylinder of known volume. The results were apparently not very satisfactory, since the estimated amount of pure radium necessary to keep the emanation constant in one cubic meter of air varied from 82×10^{-12} to 287×10^{-12} gram. The smaller value was obtained from a relatively small cylinder out of doors, the other from a large abandoned water tank indoors. The same higher value was reached by both cylinders indoors. Subsequent experiments by the same author[‡] emphasized the objections to the active deposit method. The maximum values were sixteen times the minimum, and furthermore this method does not furnish direct proof of the presence of radium emanation. Eve has recently[§] described a rather complicated new method of determining directly the amount of radium emanation in the atmosphere. This method depends upon the discovery made by Rutherford that radium emanation is readily absorbed by specially prepared cocoanut charcoal. The maximum values obtained by the absorption method were seven times the minimum, ranging from 18×10^{-12} to 127×10^{-12} gram of radium for each cubic meter of air, the probable average value being 80×10^{-12}. The well-known experiments of Rutherford and Soddy on the condensation of radium emanation suggested the possibility of a quantitative separation of the emanation from the atmosphere by means of liquid air. The qualitative separation was indeed accomplished in 1903 by Ebert.[‖] In my experiments, undertaken at the suggestion of Professor H. N. McCoy, air drawn from out of doors at ground level was passed through a purification train composed of KOH solution, H_2SO_4, $CaCl_2$, and solid KOH, and then through a coil of copper tubing immersed in liquid air, and was finally collected in aspirators made of carboys of known capacity. The coil was made of copper tubing with an outside diameter of $3{\cdot}2^{mm}$ and walls $0{\cdot}5^{mm}$ in thickness. This was wound concentrically about an axis in such a way as to allow ample space between the turns so that every part of the coil would be completely bathed in the cooling liquid.

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[*] Physik. Zeitschr., ii, 590, 1901.

[†] Phil. Mag., x, 98, 1905.

[‡] Phil. Mag., xiv, 724, 1907.

[§] Loc. cit.

[‖] Sitzb. Akad. Wiss. München, xxxiii, 133, 1903.

The entire coil occupied 75^{cc} of space and could be easily kept submerged in liquid air in a small vessel. Two hundred liters of dry air, free from carbon dioxide, could be drawn through the coil at a moderate rate in six hours. At the end of that time the coil was allowed to heat up and the volatilized emanation was transferred to a standardized gas electroscope. This was made of an air-tight brass cylinder of about one liter capacity, supporting a gold-leaf system. This electroscope has been in use by Professor McCoy for more than two years and has a very small, almost constant natural leak of about 0·148 divisions per minute (whole scale 100 divisions), when exhausted and refilled with fresh dry air. The electroscope was standardized by the method described by McCoy and Ross,* which consisted in observing the rate of discharge caused by the emanation from a portion of a mineral containing a known amount of uranium. This activity observation was made just 3¼ hours after the separation of the emanation from the mineral and 3 hours after its introduction into the electroscope The amount of radium associated with one gram of uranium in a mineral was taken as $3{\cdot}4\times10^{-7}$.†

The results of four experiments calculated on the basis of the amount of radium necessary to maintain the emanation constant in one cubic meter of air are as follows:

(1) 86×10^{-12} gram radium.
(2) 58×10^{-12} " "
(3) 45×10^{-12} " "
(4) 200×10^{-12} " "

These results seem to show a considerable variation in the amount of emanation in the air at different times; similar variations were found by Eve both by the excited activity method as well as by that in which the emanation was separated by means of charcoal. It was possible, however, that the variations in my results were due to incomplete condensation of the emanation. To decide this question, a second coil of tubing exactly like the one described above was joined to the first; both coils were immersed in liquid air, and purified outside air was run through the two coils in series at the same rate as in the four experiments above described. The emanation in the first coil corresponded to 51×10^{-12} gram of radium per cubic meter. *The second coil did not contain a trace of emanation.* This experiment clearly proved that the first coil condensed all the emanation in the air that passed through it, and showed conclusively that the observed variations were really due to variations in the amount of emanation in the air at different times. Such being the case, simultaneous duplicate determinations of the amount of radium emanation in the air

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* J. Am. Ch. Soc., xxix, 1700, 1907. † Boltwood, this Jour., xxv, 296, 1908.

should yield identical results. Such duplicate determinations were carried out by dividing the air current which had passed through the purification train and passing each half through a separate coil. In this way equal volumes of air passed through the coils simultaneously under exactly similar conditions. When corrections for the lapse of time between the observations on the contents of the coils were made, it was found that each had collected emanation corresponding to 131×10^{-12} gram of radium. This furnished additional proof that the method can be relied upon for quantitative results. As a mean of all my experiments the amount of radium necessary to produce the observed amount of emanation per cubic meter of air is $96 \times 10^{\ 12}$, or nearly 10^{-10} gram. This is about 25 per cent higher than the mean value found by Eve by the charcoal absorption method. The difference may easily be due to the variations in the quantity measured. Neither method is, however, entirely above criticism. It seems that aside from the rather lengthy and complicated nature of Eve's experiments there are two possible sources of error. One is that Eve assumes in his calculations that increasing the amount of emanation in the air three- or fourfold by the introduction of a standard radium solution does not affect the fraction of the emanation absorbed by the charcoal. This has not been tested experimentally. The other is the fact, not taken into account, that the emanation is not completely removed from a radium solution by the bubbling method. The application of this correction, however, would reduce Eve's results to a still lower value. Perhaps some of the difference between our results may be accounted for by the fact that in Eve's experiments the air was taken at a level of the fourth floor of a building, while in the experiments described here the air was taken at the earth's level. In my own experiments the fact that the second coil, after the passage of the air through the first, did not contain an amount of emanation detectable by our electroscope only proves that under the conditions of the experiment the first coil collected all the emanation capable of condensation at the temperature of liquid air. The complete condensation is limited only by the value of the vapor pressure of radium emanation at the temperature of liquid air. The experiment of Rutherford and Soddy* indicates that the vapor pressure below the condensation point is practically zero, while Ramsay† observed luminous bubbles passing down the walls of the vacuum tube while exhausting a vessel containing the frozen emanation. This would indicate an appreciable vapor pressure even at the temperature of liquid air.

The net results of all experiments show that the amount of

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* Loc. cit.

† J. Chem. Soc., xci, 932, 1907.

emanation in the air varies between rather wide limits from time to time and notably with atmospheric conditions. The high value obtained in my fourth experiment is without doubt due to the fact that that determination was made immediately after a heavy rain and general thaw, following several weeks of freezing weather with an unusual covering of snow on the ground. Probably the accumulated emanation was suddenly liberated by the rapid melting of the snow and consequent softening of the earth's crust. It is of interest to note that experiment (5) was made during a prevailing high barometric pressure, and experiment (6) during a low pressure. The difference in the barometric readings on the two dates amounted to 20^{mm} of mercury. The other weather conditions were normal. A complete study was made of the activity curve of the emanation collected in experiment (4), which proved it to be identical with that of the radium emanation. The activity reached the maximum value in about three hours after introduction into the electroscope and decreased in the usual way to half value in about 3·5 days. This showed that the active material consisted only of radium emanation. The conditions of the experiment eliminated the possibility of introducing into the electroscope any thorium emanation which may have been condensed in the copper coil, since only a few minutes are required for thorium emanation to decay to a very small fraction of its initial value. The following table indicates the course of the activity curve of the emanation in experiment (4). The different times are placed in column (1), and in column (2) are the corresponding activities in scale divisions of the graduated eyepiece passed over by the gold-leaf per minute. The activities are corrected for the natural leak of the electroscope.

(1)	(2)	
11 min.	·761	
60 "	·852	
126 "	·963	
180 "	1·100	max. activity.
19 hours	·927	
2 days	·703	
2·8 "	·604	
3·3 "	·546	
3·82 "	·490	

Conclusions.

The results of these experiments show that by cooling atmospheric air to the temperature of liquid air the radium emanation in it can be completely condensed and its amount accurately determined. Six measurements made at Chicago showed that the average amount of radium emanation per cubic meter of air could be maintained by $1·0 \times 10^{-10}$ gram of radium.

Kent Chemical Laboratory, University of Chicago, May 20, 1908.

Art. XIV.—*The Determination of Small Amounts of Barium in Rocks*; by Ralph W. Langley.

In the usual methods of rock analysis, barium is determined in a separate sample, and no correction is made for its possible interference in the main analysis. I wish to show in this article that it is possible to determine barium as sulphate in the main analysis for silica and bases, by precipitating with sulphuric acid immediately after the separation of silica. The details of this method are as follows:

The filtrate from the silica is diluted to a volume of about 400^{cm^3}, and ammonium hydroxide added until most of the hydrochloric acid is neutralized. The solution is then heated to boiling, and about 2^{cm^3} of 25 per cent sulphuric acid is added and the solution allowed to stand for about ten hours. Barium sulphate separates and is filtered on a small filter, the filter paper burned in a platinum crucible, and the residue dissolved in about 5^{cm^3} of concentrated sulphuric acid by warming over a free flame. As soon as all or nearly all of the barium sulphate has dissolved, the solution is cooled and poured into about 100^{cm^3} of water. When the barium sulphate has precipitated, it is filtered and weighed as usual. It is best to allow the solution to stand for ten hours before filtering. The second filtrate from barium sulphate usually contains iron and should be added to the first filtrate. From this point the subsequent determinations may be made as usual.

To test the method, an analysis was first made on a gabbro rock free from barium. The methods used were those of the geological survey. The results are the average of two or more determinations. One gram of material was used for each analysis. The high figure for titanium oxide led to its repeated determination, using two standard solutions, one prepared from titanium oxide and one from a crystal of rutile. The results are as follows:

SiO_2	50·75
H_2O	0·56
FeO	8·13
Fe_2O_3	2·08
TiO_2	3·05
Al_2O_3	17·31
CaO	6·77
MgO	3·48
K_2O	2·87
Na_2O	4·14
	99·14

P_2O_5, MnO, Cl, and F were present in small amounts and were not determined. Ba, Sr, S, SO_3 and CO_2 were absent.

To determine the influence of barium upon the results, four samples of this rock of one gram each were taken. To each was added an amount of $BaCl_2.2H_2O$ equivalent to five milligrams of barium oxide. The material was fused with sodium carbonate and the analyses carried on in the usual manner up to and including the separation of silica. In the filtrates from two of the silica precipitates, barium was separated by the method previously outlined. The other two analyses were conducted as usual without regard to barium. The percentage results are as follows. In column five the results obtained with the original sample free from barium are given for comparison.

	Barium removed		Barium not removed		Barium absent
$Fe_2O_3+Al_2O_3+TiO_2$ ----	---	31·68	31·39	---	31·47
BaO-----	0·53	0·56	----	---	----
CaO-----	6·69	---	6·73	6·81	6·77
MgO ----	3·46	3·57	3·72	3·77	3·48

It appears that the only determination affected by this amount of barium is that of magnesium oxide. The average of the two determinations of magnesium oxide made without removing barium is 0·27 per cent higher than in the original material. Assuming that barium is precipitated as phosphate [$Ba_3(PO_4)_2$] and weighed with the magnesium pyrophosphate in the determination of magnesium oxide, the product of the factor for converting magnesium pyrophosphate to magnesium oxide, and the weight of barium phosphate derived from five milligrams of barium oxide, equal 0·0024 grams. This accounts for the fact that the magnesium oxide figure is only 0·27 per cent too high when 5 milligrams of barium oxide are present. The presence of barium did not affect the accuracy of the determination of calcium oxide. The method for separating barium gives accurate results, and introduces no errors into the other determinations. The purification of barium sulphate by solution in concentrated sulphuric acid is necessary. In one of the determinations the weight of barium sulphate plus impurities before purification corresponded to 0·8 per cent instead of 0·5 per cent of barium oxide.

I wish to thank Prof. H. W. Foote for his advice.

Sheffield Chemical Laboratory,
New Haven, Conn., May, 1908.

ART. XV.—*The Heat of Combination of Acidic Oxides with Sodium Oxide, and the Heat of Oxidation of Chromium*; by W. G. MIXTER.

[Contributions from the Sheffield Chemical Laboratory of Yale Univ.]

IT is the purpose of the writer to accumulate data on the heat effect of the union of acidic oxides with sodium oxide, and to determine if the position in the Periodic System and the magnitude of the atomic weight of an element have a marked influence on this heat effect. Much has been accomplished by Thomsen, Berthelot and others who have derived the heat of formation of salts from the observed heat of neutralization in solution—a method not applicable in all cases to salts which hydrolyse largely. The reaction with sodium peroxide avoids errors due to hydrolysis and gives fairly accurate results, as shown in a previous paper[*] in which $2Na_2O_2, C_2 = 133500^c$ was the observed heat and 132500^c that derived from Thomsen's data. As a test of the method two determinations were made and in each rather more than two grams of rhombic sulphur were burned in a bomb with an excess of sodium peroxide. The heat effect for one gram was 5275^c and 5267^c respectively; mean 5271^c and for 32 grams of sulphur, 168670^c. The heat effect of Na_2O, SO_3 is derived thus:—

$$\begin{array}{rcr} 3Na_2O_2 , S & = & 168700^c \\ 3Na_2O , 3O & = & 58200^c \\ \hline Na_2O , S , 3O & = & 226900^c \\ S , 3O & = & 103200^{c}\dagger \\ \hline Na_2O , SO_3 & = & 123700^c \end{array}$$

From Thomsen's data we have

$$\begin{array}{rcr} 2Na , S , 4O & = & 328590^c \\ 2Na , O & = & 99760^{c}\ddagger \\ S , 3O & = & 103200^c \\ \hline Na_2O , SO_3 & = & 125630^c \end{array}$$

Thomsen used Bekétoff's result for $2Na , O$; deForcrand[§] considers it too high and that 91000^c is probably more accurate. The calculated heat effect of Na_2O , SO_3 will not be changed by using this number.

S. W. Parr[||] mentioned that oxygen is sometimes liberated in combustion with sodium peroxide and the writer has found

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[*] This Journal, xxiv, 134.

[†] Thomsen, Thermochemische Untersuchungen, ii, 254.

[‡] Ibid., iii, 232.

[§] C. R., cxxvii, 1449.

[||] J. Am. Chem. Soc., xxix, 1606.

that it is necessary to allow for oxygen taken up or set free. The correction of $1{\cdot}2^c$ for 1 milligram is based on the heat of formation of sodium peroxide from the oxide which according to deForcrand* is 19390^c. For oxygen liberated there is a loss of heat which is to be added, and for oxygen absorbed the gain is to be subtracted from the heat observed. The best way to find the change in the oxygen content of the bomb is to connect it after a combustion with a manometer. To avoid excessive detail in the data given of the work only the heat equivalent of the oxygen liberated or taken up is stated. Most of the work was done with a bomb of 500^{cc} capacity and in the work on chromium the oxygen correction was large. To obviate the correction or make it insignificant a sterling silver bomb of 100^{cc} capacity was made. It proved to be admirably adapted for calorimetric work with sodium peroxide. The water equivalent of this bomb and calorimeter can was 109^c. The large bomb was used in the experiments in which the water equivalent was over 3200 grams, and the small one in those in which it was less than 3100 grams. When a molten mass is in contact with the cold bomb it solidifies at once and the combustion is not complete. Hence it is better to put the peroxide mixture into a thin silver cup which is in contact with the inner surface of the bomb at only a few points. In order to make ignition certain the bomb was filled with oxygen, as it was found that with air in it the burning iron often failed to start the combustion. The carbon used is the finely divided form made from acetylene and the heat effect of its reaction with sodium peroxide is taken as 11100^c† per gram of carbon. The carbon gives the temperature needed to effect the combustion of other substances and also reduces the peroxide to the sodium oxide required in the reaction with an acidic oxide. The initial temperature of the experiments was between 18° and 19°.

Boric Oxide.

The heat effect of the combination of boric oxide with sodium oxide has been determined. The oxide used in the experiments, made by fusing boric acid in a platinum dish, was pulverized and weighed in a stoppered bottle. It was exposed to the air as short a time as possible on account of its hygroscopic character. The reaction of boric oxide on an excess of sodium peroxide yields the orthoborate thus:

$$3Na_2O_2 + B_2O_3 = 2Na_3BO_3 + 3O$$

No perborate results, as shown by the following experiment:

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* C. R., cxxvii, 574.

† This Journal, xix, 434.

A mixture of 1·314 gram of boric oxide and 5 grams of sodium peroxide was heated in an ignition tube. The loss in oxygen was 0·950 gram; calculated 0·901 gram. Were perborate only formed no oxygen would have been liberated, and if metaborate was the product only one-third as much oxygen would have been set free.

Experiments.

	1	2	3	
Boric oxide	1·269	1·858	1·8862	grams
Carbon	0·661	1·080	1·0384	"
Sodium peroxide	15·	20·	20·	"
Water equivalent of system	3435·	3465·	3431·	"
Temperature interval	2·679°	4·280°	4·149°	
Heat observed	9202^{c}	14830^{c}	14235^{c}	
Heat of oxidation of carbon	-7337^{c}	-11988^{c}	-11526^{c}	
Heat of oxidation of iron for ignition	-80^{c}	-64^{c}	-80^{c}	
Heat absorbed by oxygen given off	$+96^{c}$	$+60^{c}$	$+131^{c}$	
	1881^{c}	2838^{c}	2760^{c}	
For 1 gram of B_2O_3 uniting with sodium oxide	1482^{c}	1522^{c}	1463^{c}	

The three results are respectively 1482^{c}, 1522^{c}, and 1463^{c}. The average is 1489 for 1 gram and 104200^{c} for a gram molecule of boric oxide reacting with sodium oxide to form sodium orthoborate.

Note on Boron.—The only thermal data on boron are those of Troost and Hautefeuille* and Berthelot,† who determined the heat of formation of boron trichloride and tribromide and the reaction of these halides with water, and from the results they calculated the heat of formation of the trioxide. Since they give no analysis of the boron used, the purity of it is doubtful. Moreover, Moissan‡ has shown that boron prepared by reducing the oxide with sodium or magnesium is not pure. He removed the magnesium which the impure boron contained by fusion with boric oxide, taking precautions to prevent formation of nitride. It may be added that while at work on boron it was learned that another investigator, whose results are not published, considers that none of the methods described in the literature yield pure boron. Some of the observations of the writer in regard to the burning of boron are interesting and

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* Ann. Ch. Phy. (5), ix, 74.

† Ann. Ch. Phy. (5), xv, 215.

‡ Ann. Ch. Phy. (7), vi, 296.

may be briefly stated. When a mixture of impure boron and carbon was burned in oxygen under pressure the boric oxide produced volatilized and condensed as a fine white powder, and considerable boron carbide was formed. Impure amorphous boron and also crystalline boron containing aluminum reacted with explosive violence with sodium peroxide. The heat of oxidation of boron may, therefore, be easily found by the peroxide method when pure boron is available.

Aluminium Oxide.

The amorphous oxide used was prepared by igniting a powdery form of hydroxide. For crystalline oxide, crystals of corundum were taken. These were pulverized in a steel mortar, the powder digested with hydrofluoric acid, then sulphuric acid was added and the mixture heated until fumes of the latter acid escaped. Then the oxide was washed. It was white and was found to be free from lime, iron and silica, and to contain a trace of magnesia. Both preparations were floated in water and only the more finely divided portions retained. In order to determine the alumina remaining after a combustion the silver vessel containing the solid product was placed in half a liter or liter of cold water. The fusion dissolved rapidly owing to the presence of sodium peroxide. After solution the silver piece was removed and an excess of nitric acid added and the alumina filtered off. It was washed first with water and then with ammonia to remove any silver chloride present. This residue of alumina was deducted from that taken for an experiment. There is nothing in the literature regarding the solubility of ignited alumina in alkaline solutions other than the statement that the more intensely the oxide is heated the slower it is taken up by alkalies. In order to learn if the residue of alumina mentioned in the experiment is likely to dissolve so as to cause an error, the following tests were made with finely divided alumina which had been heated in a platinum crucible over a large blast lamp. In one test 4 grams of alumina and 20 grams of sodium peroxide were mixed and about 400^{cc} of hot water were slowly poured upon the mixture. The violent reaction between the peroxide and water gave at once a boiling concentrated solution of sodium hydroxide. After a few minutes an excess of nitric acid was added and the solution filtered. The alumina found in the filtrate was 2·5 per cent of the quantity taken. In another test about the same quantities of the mixed oxides were added to the surface of warm water. In this case no alumina went into solution. Since the solid residues from the combustions were chiefly sodium carbonate and aluminate, and contained much less sodium peroxide and alumina than used in the tests mentioned, it is evident that any error due to solubility of alumina is insignificant. Moreover, varying portions of sodium peroxide do not affect thermal results.

Experiments.

	1	2
Aluminium oxide (amorphous)	3·357 grams	4·313 grams
“ “ in residue	—·026 “	—·160 “
“ “ reacting	3·331 “	4·153 “
Carbon	1·218 “	1·294 “
Sodium peroxide	21· “	25· “
Water equivalent of system	3528· “	3559· “
Temperature interval	4·245°	4·479°
Heat observed	14977^c	15941^c
“ of oxidation of carbon	—13520^c	—14363^c
“ “ “ “ iron	—60^c	—60^c
	1397^c	1518^c
For 1 gram of amorphous alumina combining with sodium oxide	419^c	365^c

	3	4
Aluminium oxide (crystalline)	4·517 grams	4·038 grams
“ “ in residue	—1·174 “	— ·854 “
“ “ reacting	3·343 “	3·184 “
Carbon	0·809 “	0·814 “
Sodium peroxide	17· “	17· “
Water equivalent of system	3087· “	3036· “
Temperature interval	3·225°	3·355°
Heat observed	9956^c	10185^c
“ of oxidation of carbon	—3979^c	9035^c
“ “ “ “ iron	—32^c	—64^c
	945^c	1086^c
For 1 gram of crystalline alumina	283^c	310^c

In experiment 3 the pressure in the bomb was 16^{cm} higher after the combustion than before, and the calculated correction for the oxygen set free was 30^c. This is not included in the result above, as changes in pressure were not observed in experiments 1, 2 and 4 with alumina. In experiments 3 and 4 about two-thirds as much carbon was used as in 1 and 2. In order to find if the ratio of the carbon to the alumina influences the result, a calorimetric test was made in which the amounts of carbon and amorphous alumina were nearly the same as in experiments 3 and 4. The result was the same as in 1 and 2, as shown in the following experiment :

Experiment 5.

Aluminium oxide (amorphous)	4·237 grams
" " in residue	−0·195 "
" " reacting	4·042 "
Carbon	0·778 "
Sodium peroxide	14·
Water equivalent of system	2947·
Temperature interval	3·484°

Heat observed	10267^{c}
" of oxidation of carbon	-8635^{c}
" " " " iron	-64^{c}
	1568^{c}
For 1 gram of amorphous alumina	388^{c}

In the reaction, $2Na_2O_2+C=Na_2CO_3+Na_2O$, 1 part of carbon produces 5 parts of sodium oxide. In the formation of sodium metaluminate according to the equation, $Al_2O_3+Na_2O=2NaAlO_2$, the ratio of the quantities of the oxides is 1 to 0·6, while for the formation of the orthoaluminate three times as much sodium oxide is required. The following table of results, giving the calories evolved for one gram of alumina and the ratio of the alumina to the sodium oxide, shows that sodium orthoaluminate could not have been formed in experiments 3, 4 and 5, as there was not sufficient sodium oxide produced to form it. It should be noted in this connection that too little oxygen was set free in the combustions to indicate any material difference in the quantity of sodium oxide formed.

No. of Exp.	Calories for 1 gram Al_2O_3	C	Al_2O_3	Na_2O formed	Na_2O required to form	
					$NaAlO_2$	Na_3AlO_3
1	419	1·2	3·3 (amor.)	6·	2·	6·
2	365	1·3	4·2 "	6·5	2·5	7·6
3	283	0·8	3·3 (crys.)	4·	2·	6·
4	310	0·8	3·2 "	4·	2·	6·
5	388	0·8	4· (amor.)	4·	2·4	7·2

It is evident that the chief product in the reactions is sodium metaluminate, but possibly mixed with other aluminates. Assuming that the reaction was essentially the same in all of the combustions, we have for the heat of combination of 1 gram of amorphous alumina with sodium oxide a mean of experiments 1, 2, and 5 of 390^{c}, and for a gram molecule $40,000^{c}$. For crystalline alumina it is $30,000^{c}$. Hence the transformation of the amorphous alumina into the crystalline form is accompanied with the heat effect of $10,000^{c}$.

Chromium.

The thermal constants of chromium are of considerable importance. In Landolt and Bernstein's Physikalisch-Chemische Tabellen, p. 439, the statement is made: Die Bildungswaerme der Chromverbindungen kann nicht angegeben werden, weil keine Reaction untersucht wurde, an der metallische Chrom betheiligt ist. Then, too, it is an interesting element to study, forming basic and acidic oxides, both of which yield stable salts. Since chromium and its sesquioxide do not burn in oxygen, it is necessary to resort to indirect methods in determining the thermal constants of chromium compounds. This has been done in solutions by Thomsen, Berthelot, and others. The sodium peroxide method is a better one, and the reactions are

$$Cr + 3Na_2O_2 = Na_2CrO_4 + 2Na_2O$$
$$Cr_2O_3 + 3Na_2O_2 = 2Na_2CrO_4 + Na_2O$$

No perchromate is formed as shown by the following result: A mixture of two grams of chromium trioxide and 6 grams of sodium peroxide was placed in an ignition tube closed with a calcium chloride tube to absorb escaping water. On heating gently the mixture glowed. The loss in weight was 0·386 gram; calculated 0·32 gram. If perchromate had been formed, less oxygen would have been given off. Moreover, it is improbable that sodium perchromate can exist in a molten mass containing sodium oxide.

To Dr. C. H. Mathewson I am indebted for a fine specimen of crystalline chromium made at the Goldschmidt factory. The metal was pulverized in a steel mortar and the powder was digested with hydrochloric acid to remove the iron. Analysis proved it to be free from aluminium and silicon and to contain 0·7 per cent of iron. The last may have been from the mortar. Metallic chromium as a very fine powder will undoubtedly burn readily with sodium peroxide, but heat was necessary to effect the reaction with that used, and carbon was therefore added to the mixtures. After a combustion the product was dissolved in water, the solution made acid with nitric acid and the metal remaining was separated and weighed.

Experiments.

	1	2	3	
Metal taken	2·000	2·5000	2·500	grams
" unburned	0·061	0·0043	0·021	"
" burned	1·939	2·4957	2·479	"
Chromium	1·925	2·4782	2·4615	"
Iron	0·014	0·0175	0·0175	"
Carbon	0·2456	0·3767	0·3800	"
Sodium peroxide	20·	20·	20·5	"
Water equivalent of system	3428·	3514·	3487·	"
Temperature interval	2·601°	3·510°	3·520°	

	1	2	3
Heat observed	8916^{c}	12334^{c}	12274^{c}
“ oxidation of carbon	−2726^{c}	−4181^{c}	−4218^{c}
“ “ “ iron in metal and for ignition	− 94^{c}	− 90^{c}	− 92^{c}
“ due to oxygen absorbed	−288^{c}	−492^{c}	−472^{c}
	5808^{c}	7571^{c}	7492^{c}
For 1 gram of chromium burning with sodium peroxide	3012^{c}	3055^{c}	3044^{c}

In the experiments 1, 2, and 3 a bomb of 500^{cc} capacity was used. As the correction for oxygen absorbed was large, a determination was made with the 100^{cc} bomb. The residue insoluble in nitric acid was collected on a Gooch filter, dried and its weight found. Next the carbon was burned off, and finally the weight of unburned chromium was obtained. The pressure in the bomb was 29^{cm} less after the combustion than before.

Experiment 4.

Metal taken	02·0520	grams
“ unburned	·0015	“
“ burned	2·0505	“
Chromium	2·0361	“
Iron	0·0143	“
Carbon taken	0·3161	“
“ unburned	0·0017	“
“ burned	0·3144	“
Sodium peroxide	15·	“
Water equivalent of the system	2984·	“
Temperature interval	3·282°	

Heat observed	9793^{c}
“ of oxidation of carbon	−3489^{c}
“ “ “ “ iron in metal	−23^{c}
“ “ “ “ “ for ignition	−26^{c}
“ due to oxygen absorbed	−52^{c}
	6203^{c}
For 1 gram of chromium	3046^{c}

Evidently the correction made for oxygen taken up in the first three experiments was correct. The results are 3012^{c}, 3055^{c}, 3044^{c}, and 3046^{c}. In the first one the correction for oxygen was not made with the care that it was in the others, and hence it is better not to include it in the final value. The mean of the other figures is 3048^{c} for the reaction of 1 gram of crystalline chromium with sodium peroxide, and for 52·1 grams it is 158800^{c}.

Chromium Sesquioxide.

Amorphous chromium sesquioxide was prepared by heating an hydroxide. The crystalline oxide was made according to Ditte's* method of melting together equal parts of pure potassium dichromate and sodium chloride until the evolution of oxygen ceased. After cooling, the soluble portion of the product was dissolved in water and the crystalline powder obtained, washed, digested with hydrochloric acid and washed again. The crystals were so small that some passed through filter paper. Under the microscope they appeared unmixed with any amorphous substance. Tested by the spectroscope the preparation proved to be free from sodium and potassium. The following results show the heat of the reaction between chromium sesquioxide and sodium peroxide:

Experiments.

	1	2	3	4	
Chromium sesquioxide	4·236	3·831	7·436	6·576	grams
" " unburned	0·062	0·018	0·805	0·097	"
" " burned	4·174	3·813	6·631	6·479	"
Carbon	0·516	0·456	0·4015	0·425	"
" not burned	0·007	0·006	0·151	0·012	"
" burned	0·509	0·450	0·2505	0·413	"
Sodium peroxide	17·	15·	21·	20·	"
Water equivalent of system	2828·	2902·	2936·	3077·	"
Temperature interval	3·047°	2·703°	2·922°	3·038°	
Heat observed	8623^c	7844^c	7579^c	9348^c	
" of oxidation of carbon	—5650	—4995	—2780	—4584^c	
" " " of iron for ignition	—16	—10	—62	—48^c	
" due to oxygen absorbed or evolved	—69	—70	+14	—30^c	
	2888	2769	5751	5686^c	
For one gram of chromium sesquioxide, reacting with sodium peroxide	692	726	867	878^c	

Crystalline sesquioxide was used in experiments 1 and 2. The results are 692^c and 726^c and a mean of 709^c for the heat of the reaction of 1 gram of crystalline chromium sesquioxide with sodium peroxide. For a gram molecule it is 108000^c.

The experiments 3 and 4 were with amorphous sesquioxide. The results are 867^c and 878^c and the mean is 872^c for the heat of the reaction of 1 gram of amorphous chromium sesquioxide with sodium peroxide. For a gram molecule it is 132000^c.

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* C. R., cxxxiv, 336.

In experiment 3 the considerable quantity of unburned substance is due to the fact that the mixture was in contact with the cold bomb and was not in an inner silver cup.

Chromium Trioxide.

The chromium trioxide was free from sulphuric acid and sufficiently pure for the purpose. It was fused, allowed to cool in a desiccator and then coarsely pulverized. A little sesquioxide remained after a combustion. The amount of trioxide equivalent to it was deducted from the trioxide taken. As the heat of oxidation of the sesquioxide to the trioxide is small the error due to reduction is insignificant. The results following show the heat effect of the combination of chromium trioxide with sodium oxide.

Experiments.

	1	2	
Chromium trioxide taken	4·000	4·782	grams
" " reduced	0·097	0·176	"
" " combined	3·903	4·606	"
Carbon	0·515	0·523	"
Sodium peroxide	10·6	16·	"
Water equivalent of system	3408·	3504·	"
Temperature interval	2·514°	2·595°	
Heat observed	8567^c	9093^c	
" of oxidation of carbon	—5676	—5805^c	
" " " " iron for ignition	—62	—62^c	
" absorbed by oxygen given off	+187	+324^c	
	3016	3550^c	
For 1 gram of chromium trioxide	773	771^c	

The mean of the two results is 772^c for 1 gram and for a gram molecule of chromium trioxide it is 77000^c.

The heat of formation of the oxides of chromium is derived from the above data, thus:

$3Na_2O_2 + Cr = Na_2CrO_4 + 2Na_2O +$ .... 158800^c
$3Na_2O + 3O = 3Na_2O_2 +$ .... 58200^c

$Na_2O + Cr + 3O = Na_2CrO_4 +$ .... 217000^c
$Na_2O + CrO_3 = Na_2CrO_4 +$ .... 77000^c

$Cr + 3O = CrO_3 +$ .... 140000^c

$3Na_2O_2 + Cr_2O_3(\text{crys.}) = 2Na_2CrO_4 + Na_2O +$ 108000^c
$3Na_2O + 3O = 3Na_2O_2 +$ .... 58200^c

$2Na_2O + Cr_2O_3 + 3O = 2Na_2CrO_4 +$ .... 166200^c
$2(Na_2O + CrO_3) = 2Na_2CrO_4 +$ .... 154000^c

$Cr_2O_3(\text{crystalline}) + 3O = 2CrO_3 +$ .... 12200^c

$2(Cr + 3O) = 2CrO_3 +$ .... 280000^c
$Cr_2O_3(\text{crys.}) + 3O = 2CrO_3 +$ .... 12200^c

$2Cr + 3O = Cr_2O_3(\text{crystalline}) +$ .... 267800^c
$2Cr + 3O = Cr_2O_3(\text{amorphous}) +$ .... 243800^c

Amorphous C_2O_3 = crystalline Cr_2O_3 + ... 24000^c

Thomsen* found for $Cr_2H_6O_6$, O_3, aq $= 2CrO_3 + 18913^c$ and Berthelot† gives Cr_2O_3 precip.$+O+$eau.$=2CrO_3$ crys.$+16400^c$. The changes in the oxidation of the hydroxide are different from those in case of the oxide and hence the above results can not be compared with that of the writer. They all, however, show that the heat of formation of chromium trioxide from the sesquioxide is small. Berthelot‡ derived from reactions in solution the following: $CrO_3+K_2O=K_2CrO_4+47800^c$. This appears to be too low when considered in connection with the 77000^c found for $Na_2O+CrO_3=Na_2CrO_4$, since the heat of formation of potassium salts is commonly greater than that of sodium salts.

Tungsten.

Metallic tungsten used in the work was prepared by reducing the oxide with dry hydrogen at the highest temperature attainable in a gas combustion furnace. Even after ten hours a little water came off, showing that the reduction was not complete. During the first hours occupied in the reduction a little ammonia was formed from the atmospheric nitrogen contained in the hydrogen, but the reduced metal was free from nitrogen. The test was made by heating a mixture of the metallic powder and soda-lime. No ammonia was given off. The tungsten present in the metallic state was determined by finding the increase in weight when a weighed amount of the metal was oxidized by heating in air and finally in oxygen. The tungsten equivalent to the oxygen taken up was 98·14 per cent. Iron was present to the extent of 0·07 per cent, leaving 1·79 per cent by difference of oxide of tungsten as WO_3. Undoubtedly only the lower oxides were present and there

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* Thermochemische Untersuchungen, ii, 464.

† Thermochemie, ii, 272.

‡ Ann. Ch. Phys. (6), i, 195.

was less than 98 per cent of metallic tungsten in the preparation, but the lower oxides give heat when oxidized. Hence we may assume without essential error that the thermal effect is proportional to the amount of tungsten, which is equivalent to the amount of oxygen taken up. After each calorimetric experiment the product in the bomb was dissolved in water and the small residue remaining was separated. It dissolved completely in nitric acid, showing that no metallic tungsten remained. The following experiments give the heat of burning tungsten in sodium per oxide:

Experiment 1.

Tungsten 8·241 × 0·9814 =	8·088	grams
Water equivalent of system	3596·	"
Sodium peroxide	21·	"
Temperature interval	2·859°	
Heat observed 3596 × 2·8593 =	10281^c	
" of oxidation of iron in tungsten and used for ignition	-157^c	
	10124^c	
For 1 gram of tungsten	1252^c	

Experiment 2.

Tungsten 8·563 × 0·9814 =	8·377	grams
Water equivalent of system	3552·	"
Sodium peroxide	25·	"
Temperature interval	3·020°	
Heat observed 35523· × 02 =	10727^c	
" of oxidation of iron in tungsten and used for ignition	-125^c	
	10602^c	
For 1 gram of tungsten	1267^c	

The average is 1260^c for 1 gram and 231200^c for 184 grams. For the heat effect of $Na_2O + WO_3$ we have

$3Na_2O_2 + W = Na_2WO_4 + 2Na_2O +$	231800^c
$3Na_2O + 3O = 3Na_2O_2 +$	58200^c
$Na_2O + W + 3O = Na_2WO_4 +$	291000^c
$W + 3O = WO_4 +$	196300^c*
$Na_2O + WO_3 = Na_2WO_4 +$	94700^c

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* Delépine et Hallopeau, C. R., cxxix, 600.

Summary.

$3Na_2O + B_2O_3 = 2Na_3BO_3 +$	104200^c
$Na_2O + Al_2O_3$(amorphous) $= 2NaAlO_2 +$	40000^c
$Na_2O + Al_2O_3$(crystalline) $= 2NaAlO_2 +$	30000^c
Al_2O_3(amorphous) $= Al_2O_3$(crystalline) $+$	10000^c
$Na_2O + CrO_3 = Na_2CrO_4 +$	77000^c
$Cr + 3O = CrO_3 +$	140000^c
$2Cr + 3O = Cr_2O_3$(amorphous) $+$	243800^c
$2Cr + 3O = Cr_2O_3$(crystalline) $+$	267800^c
Cr_2O_3(crystalline) $+ 3O = 2CrO_3 +$	12200^c
Cr_2O_3(amorphous) $+ 3O = 2CrO_3 +$	36200^c
$Na_2O + WO_3 = Na_2WO_4 +$	94700^c

The results given have been obtained with substances at hand and it is the intention to complete the work as far as possible on the fourth, fifth, and sixth groups.

ART. XVI.—*Concerning Certain Organic Acids and Acid Anhydrides as Standards in Alkalimetry and Acidimetry;* by I. K. PHELPS and L. H. WEED.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxix.]

IN a former paper* from this laboratory it has been shown that, with cochineal as an indicator, succinic acid may be used as a standard for a decinormal ammonium hydroxide solution quite as accurately as may a decinormal solution of hydrochloric acid, the standard of which is determined gravimetrically as the silver chloride. In this paper results are given which show that, in presence of phenolphthalein as an indicator, pure sodium hydroxide in solution and also pure barium hydroxide in solution may be determined similarly with succinic acid, succinic anhydride, malonic acid, benzoic acid, phthalic acid and phthalic anhydride, as standards. And, further, it is shown that these organic acids and acid anhydrides react with these alkaline solutions so that each may be used as a standard in acidimetry and alkalimetry with the same exactness that is found when these alkaline solutions are titrated in the well established manner with decinormal hydrochloric acid, standardized gravimetrically as silver chloride.

For the work given here a solution of hydrochloric acid was made up approximately decinormal by diluting the chemically pure acid of commerce in the usual manner. The exact strength of the hydrochloric acid solution was determined by precipitating definite amounts of it in a platinum dish, in some cases, and in a glass beaker, in others, by an excess of silver nitrate, in presence of a few drops of dilute nitric acid. In each case the precipitate of silver chloride was allowed to stand for twenty-four hours before filtering on a weighed asbestos felt in a perforated platinum crucible. The volume in which the silver chloride was precipitated was such that after the precipitation was made it amounted to about 250 cubic centimeters.

The sodium hydroxide solution was made up to correspond approximately to the hydrochloric acid solution, by diluting with distilled water, freshly boiled, pure sodium hydroxide, prepared by the action of water vapor on metallic sodium according to the method of Küster.† The barium hydroxide was prepared pure by crystallizing twice commercial barium hydroxide out of hot water, washing the crystals after each purification with alcohol. A solution, approximately decinormal, was made by dissolving these crystals in a suitable amount

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* This Journal, xxiii, 211.

† Zeitschr. anorg. Chem., xli, 474.

of water and filtering into a closed bottle before diluting with freshly boiled distilled water. Both the sodium hydroxide solution and the barium hydroxide solution were kept in closed bottles, each connected with a three-way-stoppered burette in the usual manner. These solutions were protected from the action of carbon dioxide in the air by soda-lime tubes.

In all the experiments recorded in the tables given below, definite portions of the organic acids and acid anhydrides, in most cases, were treated with distilled water and the solution of sodium hydroxide or barium hydroxide was introduced into these solutions by carefully drawing from the burette until the appearance of color in the solution, due to the presence of phenolphthalein as indicator, showed the reaction to be complete. In a few cases, the treatment was special, as is described.

Pure succinic acid was obtained by boiling succinic ester, whose purity was established by the fact that it distilled within one-fifth of a degree, on a return condenser for four hours with water containing a few drops of nitric acid. This solution was evaporated to crystallization and the solid product,

TABLE I.

No.	Succinic acid grm.	Succinic anhydride grm.	HCl value of NaOH used grm.	HCl value of BaO_2H_2 used grm.	Theory in terms of HCl grm.	Error in terms of HCl grm.
I	0·2000	----	0·1236	----	0·1235	·0001 +
II	0·2000	----	0·1238	----	0·1235	·0003 +
III	0·2000	----	0·1237	----	0·1235	·0002 +
IV	0·2000	----	0·1236	----	0·1235	·0001 +
V	0·2000	----	0·1236	----	0·1235	·0001 +
VI	0·2000	----	0·1237	----	0·1235	·0002 +
VII	0·2000	----	0·1237	----	0·1235	·0002 +
VIII	0·2000	----	0·1237	----	0·1235	·0002 +
IX	0·2000	----	0·1237	----	0·1235	·0002 +
X	0·2000	----	0·1237	----	0·1235	·0002 +
XI	0·2000	----	----	0·1238	0·1235	·0003 +
XII	0·2000	----	----	0·1237	0·1235	·0002 +
XIII	0·2000	----	----	0·1235	0·1235	·0000 ±
XIV	0·2000	----	----	0·1236	0·1235	·0001 +
XV	----	0·2000	0·1458	----	0·1458	·0000 ±
XVI	----	0.2000	0·1458	----	0·1458	·0000 ±
XVII	----	0·2000	0·1459	----	0·1458	·0001 +
XVIII	----	0·2000	0·1458	----	0·1458	·0000 ±
XIX	----	0·2000	----	0·1457	0·1458	·0001 —
XX	----	0·2000	----	0·1456	0·1458	·0002 —
XXI	----	0·2000	----	0·1459	0·1458	·0001 +
XXII	----	0·2000	----	0·1458	0·1458	·0000 ±

after the removal of the mother liquor by filtering, was recrystallized from distilled water. After these crystals had dried in the open air to constant weight, it was found that on standing over sulphuric acid in a desiccator the weight remained unchanged. For the preparation of succinic anhydride, commercial succinic acid was treated with an excess of acetyl chloride and heated on a water bath with a return condenser at 60°, as long as bubbles of gaseous hydrochloric acid were evolved from the liquid. The material, which separated out on cooling, was recrystallized from ethyl acetate. These crystals of succinic anhydride were then washed with absolute alcohol and were dried to constant weight over sulphuric acid in a desiccator.

The succinic acid used in experiments VI, VII, and VIII of Table I had been dried for more than a year in a desiccator containing sulphuric acid, while that used in experiments IX and X of the same table had been dried for the same length of time over calcium chloride in a desiccator. It is evident from these experiments that succinic acid dried in desiccators over sulphuric acid or calcium chloride for long periods of time is unaffected.

Owing to the considerable length of time that is taken by succinic anhydride to dissolve in water even in the presence of some alkali, experiments XX and XXII of Table I were slightly modified. In these the solution was heated until the anhydride completely dissolved before any of the alkaline hydroxide was added.

Malonic acid was prepared pure by heating for some hours between 50° and 60° on a return condenser malonic ester, which boiled between limits of two-tenths of a degree, with water in the presence of a few drops of nitric acid. The volume was then concentrated, keeping the temperature of the solution below 60° until crystallization began, the crystals

TABLE II.

No.	Malonic acid grm.	HCl value of NaOH used grm.	HCl value of BaO_2H_2 used grm.	Theory in terms of HCl grm.	Error in terms of HCl grm.
I	0·2000	0·1404	----	0·1402	·0002 +
II	0·2000	0·1403	----	0·1402	·0001 +
III	0·2000	0·1402	----	0·1402	·0000 ±
IV	0·2000	0·1401	----	0·1402	·0001 —
V	0·2000	----	0·1401	0·1402	·0001 —
VI	0·2000	----	0·1400	0·1402	·0002 --
VII	0·2000	----	0·1402	0·1402	·0000 ±
VIII	0·2000	----	0·1400	0·1402	·0002 —

filtered off and recrystallized out of boiling water. The pure malonic acid was then allowed to come to constant weight over sulphuric acid in a desiccator.

To obtain pure benzoic acid, benzoic ester was treated with sodium hydroxide in excess, and acidified with hydrochloric acid. The benzoic acid thus precipitated was crystallized twice from water and dried to constant weight in a desiccator over sulphuric acid.

TABLE III.

No.	Benzoic acid grm.	HCl value of NaOH used grm.	HCl value of BaO_2H_2 used grm.	Theory in terms of HCl grm.	Error in terms of HCl grm.
I	0·2000	0·0598	----	0·0597	·0001 +
II	0·2000	0·0599	----	0·0597	·0002 +
III	0·2000	0·0597	----	0·0597	·0000 ±
IV	0·2000	0·0598	----	0·0597	·0001 +
V	0·2000	----	0·0598	0·0597	·0001 +
VI	0·2000	----	0·0597	0·0597	·0000 ±
VII	0·2000	----	0·0597	0·0597	·0000 ±
VIII	0·2000	----	0·0597	0·0597	·0000 ±

In all of the experiments in Table III, alkali in amount nearly sufficient to neutralize the acid was run into the flask, which was then heated. This aided materially in securing the solution of the benzoic acid in the water and did not necessitate raising the solution to the boiling point.

TABLE IV.

No.	Phthalic acid grm.	Phthalic anhydride grm.	HCl value of NaOH used grm.	HCl value of BaO_2H_2 used grm.	Theory in terms of HCl grm.	Error in terms of HCl grm.
I	0·2000	----	0·0880	----	0·0878	·0002 +
II	0·2000	----	0·0880	----	0·0878	·0002 +
III	0·2000	----	0·0879	----	0·0878	·0001 +
IV	0·2000	----	0·0878	----	0·0878	·0000 ±
V	0·2000	----	----	0·0876	0·0878	·0002 −
VI	0·2000	----	----	0·0877	0·0878	·0001 −
VII	0·2000	----	----	0·0878	0·0878	·0000 ±
VIII	0·2000	----	----	0·0879	0·0878	·0001 +
IX	----	0·2000	0·0986	----	0·0985	·0001 +
X	----	0·2000	0·0985	----	0·0985	·0000 ±
XI	----	0·2000	0·0986	----	0·0985	·0001 +
XII	----	0·2000	0·0987	----	0·0985	·0002 +
XIII	----	0·2000	----	0·0986	0·0985	·0001 +
XIV	----	0·2000	----	0·0985	0·0985	·0000 ±
XV	----	0·2000	----	0·0986	0·0985	·0001 +
XVI	----	0·2000	----	0·0987	0·0985	·0002 +

Phthalic acid was prepared by boiling in distilled water some commercial phthalic anhydride. The solution was filtered while still hot; the crystalline product obtained on cooling was separated by filtration, air-dried, and finally dried to constant weight in a desiccator over sulphuric acid. The phthalic anhydride was prepared in a state of purity by distilling *in vacuo* the phthalic anhydride of commerce. The product obtained was dried to constant weight in a desiccator containing sulphuric acid.

In Table IV, experiments II and VIII alone were carried on at ordinary temperatures. In the other experiments in this table the titrations were all performed after heating the solution until the phthalic acid or the phthalic anhydride used had entirely dissolved.

It is evident from the results recorded in the four tables that succinic acid, succinic anhydride, malonic acid, benzoic acid, phthalic acid and phthalic anhydride may be used with great exactness as standards for decinormal solutions of sodium hydroxide and of barium hydroxide. As a standard for a solution of barium hydroxide, these organic acids and acid anhydrides are even more accurate in our experience than the determination of the barium hydroxide solution gravimetrically as the barium sulphate. In the various tables are given results which show the accuracy with which barium hydroxide may be standardized by the different organic substances when compared with the standard of decinormal hydrochloric acid established as the silver chloride. This same solution of the barium hydroxide which gave a value of 0·006396 grm. per cubic centimeter in terms of hydrochloric acid when standardized against the organic acids and acid anhydrides, gave a value of 0·006430 grm. per cubic centimeter in terms of hydrochloric acid when standardized by precipitating and weighing as the barium sulphate, by the usual procedure for the determination of barium.

As standards in alkalimetry and acidimetry, these organic acids and acid anhydrides, in pure state, are equally as accurate as the best previous standard—hydrochloric acid determined gravimetrically as the silver chloride. The most serviceable of these organic substances tested are those most readily soluble in water—succinic and malonic acids—although they are no more accurate than the other organic acids and acid anhydrides, as is shown by the results given in the tables. Since these substances can be readily prepared in a known state of great purity, their serviceability as most accurate standards is evident.

ART. XVII.—*A Comparison between Succinic Acid, Arsenious Oxide, and Silver Chloride as Standards in Iodimetry, Acidimetry, and Alkalimetry;* by I. K. PHELPS and L. H. WEED.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxx.]

THE use of an excess of a mixture of an iodide and an iodate has been suggested by several as a most exact and convenient method for determining quantitatively various acids in alkalimetry and acidimetry. Kjeldahl* suggested the use of these reagents for determining nitrogen as ammonia in organic substances. Later Furry† showed that the conditions of concentration affected the end-point of this reaction. In very dilute solutions there was an after-coloration which he showed to be due to the incomplete action of the mineral acid rather than to the action of carbonic acid in solution. Gröger‡ showed the applicability in alkalimetry and acidimetry of the iodide-iodate mixture for determining decinormal solutions of acids and of alkaline hydroxides, carbonates, and sulphides. In the case of the acids, he treated directly with an excess of the neutral iodide-iodate mixture and measured the iodine set free by titration, in presence of starch as an indicator, with sodium thiosulphate, standardized either against a weighed amount of free iodine or against the iodine set free by the action of an excess of hydrochloric acid and of iodate-free potassium iodide upon a weighed amount of pure potassium iodate in solution. In the case of the alkaline hydroxides, carbonates, and sulphides, the solutions were treated with an excess of standard mineral acid and then this excess was determined in the manner described above. The comparison was shown between the results so obtained and those given by direct titration of the solution of the alkalies against decinormal sulphuric acid, in presence of litmus and of phenolphthalein as indicators, and, for the acids, by similar titration with a decinormal potassium hydroxide solution. The agreement was good except in the case of the carbonates where the iodometric results are low, even when the solutions were allowed to stand for thirty minutes before completing the titration. In a later paper§ Gröger suggested pure potassium iodate as a standard in iodimetry, acidimetry, and alkalimetry. The results are good but the difficulty in using the process for practical work is not only the necessity of obtaining pure potassium iodate but also the necessity of using potassium iodide free from iodate.

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* Zeitschr. analyt. Chem., xxii, 366.
† Amer. Chem. Jour., vi, 341.
‡ Zeitschr. angw. Chem., 1890, 353.
§ Zeitschr. angw. Chem., 1890, 385.

The practical difficulty usually found in the use of arsenious oxide as a standard in iodimetry lies, in our experience, in the fact that in most cases the purest resublimed arsenious oxide does not always give a clear solution when treated with an alkaline hydroxide or bicarbonate. To whatever cause this insoluble residue may be due—to a slight action of the alkaline solution upon the glass or to some impurity in the alkaline hydroxide or bicarbonate used—it is in itself sufficient to make desirable, for accurate work, the possibility of checking results obtained with arsenious oxide as a standard.

It has been shown in former papers* from this laboratory that succinic acid may be used, in presence of cochineal as an indicator, as a standard for the exact determination of a decinormal solution of ammonium hydroxide, and, also, that succinic, malonic, benzoic, and phthalic acids, as well as the anhydrides of succinic and phthalic acids, may also be used, with phenolpthalein as an indicator, as standards for decinormal solutions of sodium hydroxide and of barium hydroxide. The results, which are given below, show that succinic acid may also be used as the standard for work in iodimetry, alkalimetry, and acidimetry, with exactly as much accuracy as the best previous standards for this work—titration against a decinormal solution of pure arsenious oxide or the gravimetric determination of a solution of hydrochloric acid as silver chloride.

For this work, solutions of hydrochloric acid and of sulphuric acid were made up approximately decinormal by diluting in the usual way the chemically pure acids of commerce. The exact strength of the hydrochloric acid solution was determined by precipitating definite amounts of the solution of hydrochloric acid, in some cases, in a platinum dish and, in other cases, in a glass beaker as silver chloride by an excess of silver nitrate in the presence of a few drops of dilute nitric acid, filtering off on asbestos under pressure in a perforated platinum crucible the precipitate of silver chloride after allowing the whole to stand in the dark twenty-four hours. The solution of sodium hydroxide was prepared by diluting pure sodium hydroxide, prepared by the method given by Küster,† with distilled water, freshly boiled. The solution of sodium hydroxide was kept in a closed bottle, connected in the usual manner with a three-way-stoppered burette. It was protected from the action of carbon dioxide in the air by soda lime tubes. The exact strength of this approximately decinormal solution was determined by titration against the standard solution of hydrochloric acid, approxi-

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* This Journal, xxiii, 211; xxvi, 138.

† Zeitschr. anorg. Chem. xli, 474.

mately decinormal, and against pure succinic acid, in the manner described in the paper to which reference has been made. The exact standard of the decinormal solution of sulphuric acid was determined by titration against the decinormal sodium hydroxide solution, in presence of phenolphthalein as indicator.

The decinormal solution of arsenious oxide was carefully made up by treating 4·9500 grams of the purest arsenious oxide of commerce, twice sublimed, in a beaker in fifty cubic centimeters of distilled water with fifty cubic centimeters of a solution containing about twelve grams of sodium hydroxide, prepared pure according to the method of Küster.* After the arsenious oxide had been dissolved by gentle warming, the solution was transferred to a standardized liter flask, by using enough distilled water in this transference to make the volume approximately 250 cubic centimeters. This was then saturated with purified carbon dioxide and diluted to a liter under proper conditions of temperature. The solution of iodine was made up approximately decinormal by dissolving iodine in an aqueous solution of potassium iodide, the exact strength of the solution being determined by titration against the standard solution of decinormal arsenious oxide, in presence of an excess of sodium bicarbonate, with starch solution made in the usual way as the indicator. The solution of sodium thiosulphate was made up approximately decinormal by dissolving in distilled water the pure sodium thiosulphate of commerce. The exact strength of this solution was determined by titrating definite portions of it against the iodine solution, using the starch solution as indicator.

In this work, potassium iodide and potassium iodate were first put into solution in such amounts as to be in excess at the end of the reaction. Definite portions of the decinormal hydrochloric acid solution were then run in from a burette, setting free the iodine. The solution of sodium thiosulphate was next added in amount slightly in excess, and this excess was determined either by adding more of the hydrochloric acid solution or by the addition of the iodine solution, until the blue color of the starch indicator showed the reaction to be complete. In all of the experiments recorded in Table I, one gram of potassium iodide was used and fifty cubic centimeters of a solution of potassium iodate, prepared by dissolving 3·3400 grams of the iodate in a liter of distilled water. Presumably on account of the presence of acid potassium iodate in the sample of iodate used, the addition of the potassium iodate solution to the potassium iodide set free a slight amount of iodine. This free iodine was removed either by boiling until

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* Loc. cit.

the characteristic color of free iodine disappeared, or by adding portions of a dilute sodium thiosulphate solution until the blue color of the starch solution introduced was bleached. In all of the experiments in this table, also, five cubic centimeters of a potato starch solution were added before the titration was begun.

TABLE I.

	HCl value of				
No.	HCl solution used grm.	$Na_2S_2O_3$ solution used grm.	Iodine solution used grm.	HCl found grm.	Error in HCl grm.
(1)	0·1074	0·1075	----	0·1075	0·0001 +
(2)	0·1074	0·1074	----	0·1074	0·0000 ±
(3)	0·1074	0·1075	----	0·1075	0·0001 +
(4)	0·0520	0·0520	----	0·0520	0·0000 ±
(5)	0·1560	0·1562	----	0·1562	0·0002 +
(6)	0·0645	0·0712	0·0068	0·0644	0·0001 —
(7)	0·0968	0·1068	0·0101	0·0967	0·0001 —
(8)	0·0645	0·0712	0·0067	0·0645	0·0000 ±
(9)	0·0968	0·1068	0·0101	0·0967	0·0001 —
(10)	0·0484	0·0534	0·0050	0·0484	0·0000 ±
(11)	0·0645	0·0748	0·0104	0·0644	0·0001 —
(12)	0·0484	0·0534	0·0050	0·0484	0·0000 ±
(13)	0·0645	0·0712	0·0066	0·0646	0·0001 +

In experiments (1) to (5) inclusive of Table I the excess of the sodium thiosulphate was determined by the addition of decinormal hydrochloric acid to color with starch, while in the other experiments the excess was determined similarly by titration against the decinormal iodine solution. In experiments (1) to (7) inclusive, the iodine set free on the addition of the potassium iodate to the potassium iodide was removed by boiling as described above. In experiments (8) to (13) inclusive of the same table, the iodine set free was removed by dilute sodium thiosulphate, which was added until the color of the starch solution present was bleached.

The solution of hydrochloric acid used to set free the iodine was standardized as silver chloride as well as against a decinormal sodium hydroxide solution, the exact strength of which was established by titrating with the organic substances as standards, as we have shown in a former paper.* It was shown also in that paper that the standards obtained by silver chloride and the organic substances are in agreement within the limits of experimental error. From an inspection of Table I, in which the action of a decinormal solution of hydrochloric acid, stand-

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* This Journal, xxvi, 138.

ardized as the silver chloride, as well as the organic substances mentioned above, is brought into comparison with decinormal solutions of sodium thiosulphate and iodine, standardized against a carefully prepared solution of arsenious oxide, it is evident that the two standards, silver chloride and the organic substances, are in agreement with the third standard, a decinormal arsenite solution made up with the precautions given above.

Further, it is evident that the incompleteness of the action of mineral acid on a mixture of iodide and iodate in dilute solution, as shown by Furry,* does not take place appreciably under the conditions used here with decinormal solutions. This is particularly striking in view of the different procedures used in the experiments recorded. When, however, the action of centinormal solutions of iodine, thiosulphate, and hydrochloric acid was tested with the iodide-iodate mixture, the phenomena observed by Furry became very apparent, comparatively wide variations in the results being obtained.

That this method of standardization in alkalimetry could also be used in the presence of carbonates is shown in Table II. In the experiments included in that table, definite portions of the decinormal solution of sodium hydroxide were first drawn from the burette. Purified carbon dioxide was then passed into this solution for different lengths of time, converting the sodium hydroxide to the carbonate or bicarbonate. The solution of sulphuric acid was then added in excess, and the carbon dioxide set free was completely driven out of the solution by boiling in a flask, trapped with the bulb-end of an ordinary calcium chloride tube, to prevent mechanical loss, the boiling being continued until the volume was reduced one-third. After cooling, the excess of acid was estimated in two ways. In experiments (1) to (4) inclusive, the excess of acid was determined by direct titration, in presence of phenolphthalein as an indicator, with the decinormal solution of sodium hydroxide. The second method of determining the excess of the sulphuric acid was used in experiments (5) to (8) inclusive. To these, after cooling, a solution, containing one gram of potassium iodide and fifty cubic centimeters of the solution of potassium iodate described above, was added, after the free iodine had been removed from this iodide-iodate solution by the addition of a dilute sodium thiosulphate solution in the presence of starch as an indicator. Definite portions of the decinormal sodium thiosulphate solution were then added in excess, and this excess was determined by titration with the decinormal iodine solution.

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* Loc. cit.

Table II.

		HCl value of					
No.	Treatment with CO_2 min.	NaOH solution used grm.	H_2SO_4 solution used grm.	NaOH solution to coloration grm.	$Na_2S_2O_3$ solution used grm.	Iodine solution to coloration grm.	Difference in terms of HCl grm.
(1)	15	0·1012	0·1306	0·0293	------	------	0·0001+
(2)	30	0·1012	0·1219	0·0205	------	------	0·0002+
(3)	15	0·1349	0·1524	0·0172	------	------	0·0003+
(4)	30	0·1349	0·1568	0·0216	------	------	0·0003+
(5)	15	0·1012	0·1306	------	0·0302	0·0013	0·0005+
(6)	30	0·1012	0·1306	------	0·0302	0·0013	0·0005+
(7)	15	0·1349	0·1742	------	0.0392	0·0004	0·0005+
(8)	35	0·1349	0·1742	------	0·0552	0·0162	0·0003+

The differences recorded in the last column of Table II show that the standard of the sulphuric acid is slightly higher than the summation of the sodium hydroxide originally taken, and of the sodium hydroxide or thiosulphate and iodine used to determine the excess of sulphuric acid. From these results it seems to appear that the differences are presumably to be attributed to two causes—the experimental error and, perhaps, a slight mechanical loss of sulphuric acid during the long boiling.

These results show that a non-volatile acid like sulphuric acid may be used with exactness to determine alkaline carbonates in either of the two ways described. The essential thing in the exact titration with a solution of sodium hydroxide, with phenolphthalein as an indicator, as is well known,* is the absence of carbonate, as is also the case in the use of the potassium iodide-iodate mixture.† This condition is easily attained by boiling, as was done in these experiments.

From these results, it may be seen that the standards of the solutions used in work in iodimetry, alkalimetry, and acidimetry may be found as exactly by titrating against certain pure organic acids as standards, as against the best known standards usually used in such work—the decinormal solution of arsenious oxide, or a decinormal solution of hydrochloric acid, standardized gravimetrically as silver chloride. Succinic acid was used as the organic acid standard in this work because of the ease with which it is prepared in a state of purity and its ready solubility in water, but it is clear from work shown in an earlier paper‡ from this laboratory that malonic, benzoic, and phthalic acids as well as the anhydrides of succinic and phthalic acids, could be used with equal exactness.

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* Küster, Zeitschr. anorg. Chem., xiii, 127.
† Gröger, Zeitschr. angw. Chem., 1890, 353.
‡ This Journal, xxvi, 138.

ART. XVIII.—*On Orthoclase Twins of Unusual Habit;* by W. E. FORD and E. W. TILLOTSON, JR.

THE orthoclase twins to be described in the following pages were collected by Prof. L. V. Pirsson during the summer of 1896, while engaged in work for the United States Geological Survey in Montana. They occurred as phenocrysts in an altered tinguaite porphyry which lay as an intruded sheet between black shales near the head of West Armell Creek in the Judith Mountains. The tinguaite sheet is described* as measuring "between ten or twelve feet in thickness with numerous immense feldspar phenocrysts, some of them being four by two by one inches across." The groundmass of the rock is fine-grained with a greenish gray color, the green tone being due to the presence of fine crystals of ægirite, while on the weathered surfaces it is spotted with numerous pits stained yellow with iron oxide. The writers desire to express to Prof. Pirsson their thanks for the opportunity to figure and describe these crystals.

The phenocrysts occur as well-developed crystals and, as has been said, are at times of considerable size. They are opaque and are frequently stained on the surface with iron oxide or colored green with a thin coating of ægirite. When broken, however, they present a glassy luster and fresh appearance. The crystal faces were too rough to admit of measurements other than those with the contact goniometer, but the forms present were easily identified in this way and by their zonal relations. They were all common forms comprising *b* (010), *c* (001), *m* (110), *z* (130), *n* (02$\bar{1}$) and *o* ($\bar{1}$11). A few crystals in the suite were untwinned and possessed a development as represented in figure 1, but for the most part the phenocrysts were twinned according to the Baveno law in which *n* (021) becomes the twinning plane. They differ markedly in habit, however, from the common form of Baveno twins in that instead of having the composition plane symmetrically placed in diagonal position through the square prism-like crystals, they are rather in the nature of contact twins having the two individuals more or less completely developed and grown together at right angles to each other without much interpenetration. Figures 2 and 3 illustrate this peculiarity of development. In these cases the division between the two individuals can be distinctly traced, and is practically a single plane. In the crystal illustrated in figure 2, the individual drawn in normal position is quite completely and symmetrically developed and the smaller

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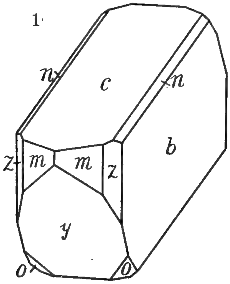
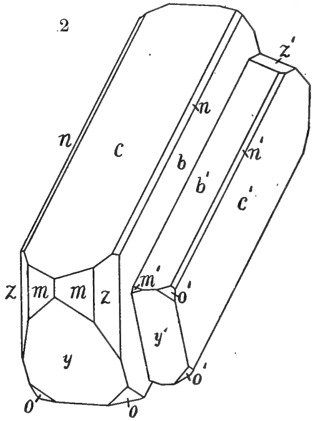
* Weed and Pirsson, U. S. G. S., Ann. Rep., 1896–7, iii, 524.

one, not so completely formed, is merely grown on to the side of the larger. The bottom plane of this twin is made up of the c $(00\bar{1})$ face of the first and the b' $(0\bar{1}0)$ face of the second individual, the division between the two being clearly recognizable because in these crystals the clinopinacoid has always a somewhat brighter luster than the base. In this case the dividing line between the two faces is almost straight. In the crystal represented in figure 3, the two individuals are more nearly equally developed, and here again the division between the two seems to be almost in the nature of a single plane. The composite face of this crystal is the one in back and to the left as the crystal is drawn and the distinction between the c and b faces is clearly

1



2



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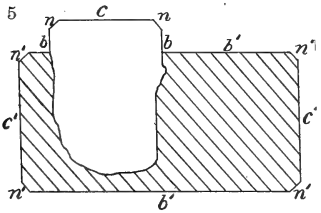

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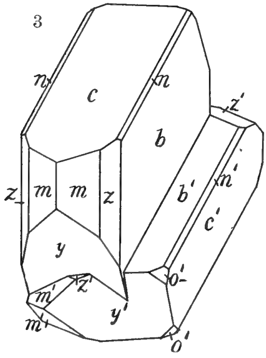

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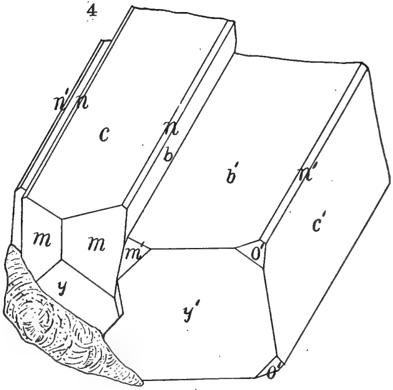

defined, as the former is coated with a thin film of green ægirite, while the latter is clean.

The crystal represented in figure 4, although in general of the same type, differs in that the individual shown in normal position is apparently set into the other, the latter in a measure surrounding the former. In order to ascertain the relations existing between the two individuals of this twin, a section was cut through the crystal along a plane at right angles to the *c* and *b* faces and close to the front of the crystal. Figure 5 shows the relationship between the two individuals along this plane as indicated by the section, the shaded portion of the figure representing that part of the crystal placed in twin position. Where the dividing line was straight and clean cut, there was a slight crack to be observed between the two parts of the twin, but elsewhere there was considerable kaolinization of the feldspar and this line became more irregular and indistinct.

The crystals were investigated both optically and chemically, in order to ascertain if they showed in these respects any unusual features which might be connected with their peculiar development. Sections were made parallel to the three pinacoids, *a* (100), *b* (010) and *c* (001). They showed that the mineral was slightly kaolinized, but not to any great extent. There was no evidence of microscopic twinning or of parallel growth of more than one feldspar. The optical orientation is that most common with orthoclase, the axial plane being perpendicular to *b* (010), $\mathfrak{a}$ inclined to the *a* axis +4° 54′, and $\rho > v$. The conformity in its optical properties to normal orthoclase is rather surprising when the large amount of soda shown to be present by the analysis is considered. The results of the analysis by Tillotson follow:

SiO_2	64·01
Al_2O_3	20·19
K_2O	10·48
Na_2O	5·37
Total	100·05

This particular occurrence of the tinguaite rock was not analyzed because of the alteration it had undergone through weathering, but a closely similar and fresh rock from Cone Butte was analyzed by Pirsson* and the percentage of the alkalies found by him agree closely with those of the present analysis. In the Cone Butte tinguaite, however, the soda was considered to belong entirely to either albite or nephelite, but in the West

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* This Journal, ii, 192, 1896.

Arnell Creek occurrence, supposing that the two magmas were alike, it would all be accounted for by the orthoclase itself. In the present analysis the somewhat disproportionately low percentage of silica is probably due to the small amount of kaolinization which the feldspar showed in the thin sections.

Drawing of the Crystals.—The crystals were drawn from a stereographic projection of their forms. There was nothing new in the methods employed, but as concrete examples of the use of the stereographic projection for the solution of such problems are seldom to be met with in the literature, a brief description of the manner of transposition of the poles of the faces from normal to twin position is here given.* According to the Baveno law of twinning the *n* (021) face becomes the twinning plane and as the angle $c \wedge n = 44° \ 56 \ 1/2'$ the angle between *c* and *c'* (twin position) becomes 89° 53′. For the

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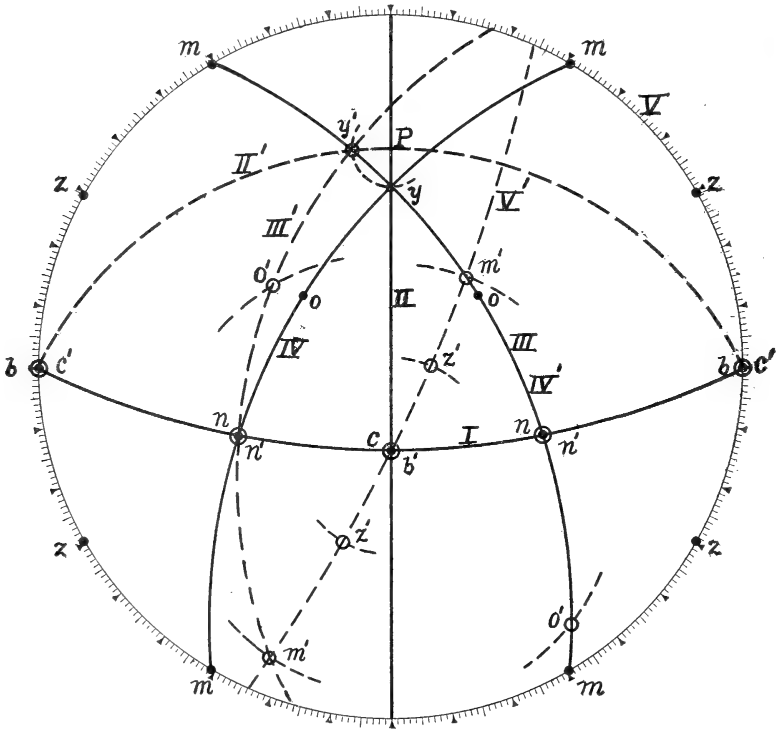

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* For a general discussion of the graphical use of the stereographic projection, see Penfield, this Journal, xi, 1, 1901.

purposes of drawing it is quite accurate enough to assume that this angle is exactly 90° and that accordingly the *c* face of the twin will occupy a position parallel to that of the *b* face of the normal individual.

Figure 6 shows the forms observed of the crystals both in normal and in twin positions, the faces in twin position being indicated by open circles and a prime mark (′) after their respective letters, while the zones in twin position are drawn in dashed lines. Starting out with the forms in normal position, the first face to transpose is the base *c*. This form, from the law of the twinning, will be transposed to *c*′ where it occupies the same position as *b* of the normal individual, and it necessarily follows that *b* itself in being transposed will come to *b*′ at the point where the normal *c* is located.

In turning therefore the crystal to the left from normal to twin position, the faces *c* and *b* travel along the great circle I through an arc of 90° until they reach their respective twin positions. We have, in other words, revolved the crystal 90° to the left about an axis which is parallel to the faces of the zone I. The pole of this axis is located on the stereographic projection at 90° from the great circle I and falls on the straight line II, another great circle which intersects zone I at right angles. This pole *P* is readily located by the stereographic protractor on the great circle II at 90° from *c*. The problem then is to revolve the poles of the faces from their normal positions about the point *P* to the left and through an arc of 90° in each case.

During the revolution the poles of the *n* faces remain on the great circle I and as the angle $n \wedge n = 90°$, the location of their poles when in twin position is identical with that of the normal position and *n*′ falls on top of *n*. We can now transpose the great circle II from its normal to its twin position, since *P* remains stationary during the revolution and we have determined the twin position of *c*. The dashed arc II′ gives the twin position of the great circle II. The twin position of *y* must lie on arc II′ and can be readily located at *y*′, the intersection of arc II′ with a small circle about *P* having the radius $P \wedge y$. It is now possible to construct the arc of the zone III in its transposed position III′, for we have two of the points, *y*′ and *n*′ of the latter, already located. By the aid of the Penfield transparent great circle protractor the position of the arc of the great circle on which these two points lie can be determined. On this arc, III′, *o*′ and *m*′ must also lie. Their positions are most easily determined by drawing arcs of small circles about *b*′ with the required radii, $b \wedge o = 63°8'$, $b \wedge m = 59°\ 22\ 1/2'$ and the points at which they intersect arc III′ locate the position of the poles *o*′ and *m*′. At the same time the corresponding points on IV′ may be located, it being noted that IV′ and III are the same arc. But one other form remains to be transposed, the prism *z*. We have already *b*′ and *m*′ located and it is a simple matter with the aid of the great circle protractor to determine the position of the great circle on which they lie. Then a small circle about *b*′ with the proper radius, $b \wedge z = 29° \ 24'$, determines at once by its intersections with this arc the position of the poles of the *z* faces.

The transposition of the faces from normal to twin position having been made, it is a simple matter to draw the crystal figures from the projection.* It may be pointed out that if it should be desired to make use of the methods of the gnomonic projection for the drawing of the figures the stereographic projection, as derived above, can be readily transformed into a gnomonic projection by doubling the angular distance from the center of the projection to each pole by the use of the stereographic protractor. But from whichever projection it is preferred to draw the figures, it is thought that the stereographic projection, with the aid of the Penfield protractors, offers the simplest method for the ready transposition of the poles of the faces from normal into twin positions.

Mineralogical Laboratory of the Sheffield Scientific School,
Yale University, New Haven, Conn., April, 1908.

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* See Penfield, this Journal, xxi, 206, 1906.

Art. XIX.—*The Palisade Diabase of New Jersey;* by J. Volney Lewis.*

The intrusive trap that forms the Palisades of the Hudson extends, with outcrops several hundred feet thick, from west of Haverstraw, N. Y., southward to Staten Island and, somewhat intermittently, westward across New Jersey to the Delaware River, an aggregate length of about 100 miles.† It is everywhere a medium- to fine-grained dark gray heavy rock, with dense aphanitic contact facies.

The typical coarser rock contains, in the order of abundance, augite, plagioclase feldspars, quartz, orthoclase, magnetite, and apatite. The first two occur in ophitic to equant granular texture, and the next two in graphic intergrowths which sometime constitute one-third of the rock; in the contact facies this micropegmatite disappears and scattering crystals of olivine occur.

A highly olivinic ledge, 10 to 20 feet thick and about 50 feet from the base of the sill, is exposed in the outcrops northward from Jersey City for about twenty miles. The olivine crystals, which constitute 15 to 20 per cent of this rock, occur as poikilitic inclusions in the augite and feldspar.

Chemically the diabase ranges from less than 50 to more than 60 per cent of silica, with corresponding variation in alumina, ferric oxide, and the alkalis, while ferrous iron, lime, and magnesia vary inversely. The augite is rich in these latter constituents and poor in alumina, giving a great preponderance of the hypersthene and diopside molecules. The feldspars range from orthoclase and albite to basic labradorite. Doubtless there is some anorthoclase since all feldspar analyses show potash.

While there is considerable range in the proportions of the minerals, augite usually comprises about 50 per cent of the rock, the feldspars about 40 per cent, quartz 5 per cent, and the ores 5 per cent, constituting a quartz-diabase, with normal and olivine-diabase facies. Basic concentration at the contacts, followed by differentiation by gravity during crystallization of the body of the sill, especially by the settling of olivine and the ores and the rising of the lighter feldspars in the earlier and more liquid stages of the magma, are hypotheses that seem to account for the facies observed and their present relations.

Microscopic characters.—In thin sections the texture of the rock is usually diabasic, or ophitic; that is, the augite fills the

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* Read before the New York Academy of Sciences April 6, 1908. Published by permission of the State Geologist of New Jersey.

† J. Volney Lewis, Structure and Correlation of the Newark Trap Rocks of New Jersey, Bull. Geol. Soc. of America, vol. xviii, pp. 195–210; also Origin and Relations of the Newark Rocks, Ann. Rept. State Geologist of N. J. for 1906, pp. 97–129.

interstices between the interlacing lath-shaped feldspars, or when greatly in excess it forms the groundmass in which the feldspars are imbedded. In the coarser-grained portions of the rock there is often developed a granitoid texture, in which the two chief minerals occur in grains of approximately equal size and of nearly equal dimensions in every direction.

Augite, the most abundant constituent, is pale green to colorless and sometimes exhibits distinct pleochroism—pale green to light yellow.* It occurs in plates up to 3 or 4 millimeters in diameter, and in irregular grains whose forms are determined by the accompanying feldspars. Crystal outlines are rarely observed. In the denser contact facies augite of two generations appears, the earlier as large plates scattered through the denser groundmass in which the augite of later crystallization forms a fine granular filling between the feldspars. Two forms of twinning often appear, both separately and in combination. That parallel to the orthopinacoid (100) usually produces paired halves, while the basal twinning (parallel to 001) is more commonly repeated in thin lamellæ, which are sometimes exceedingly minute.

Plagioclase, the chief feldspar and the second constituent in abundance, occurs in characteristic lathlike forms, ranging up to 2 millimeters in length with a breadth one-fifth to one-third as great. In the coarse textures of the granitoid facies these dimensions become more nearly equal, and diameters of 3 to 4 millimeters are often observed. Often the plagioclase presents complete crystal outlines, but very commonly the terminal planes are lacking, the elongated crystals abutting irregularly against each other. They are made up of thin twinning lamellæ, chiefly according to the albite law, but pericline and Carlsbad twinning also occur. Zonal structure is quite commonly developed, and fringing the extreme acid borders a graphic intergrowth of quartz and orthoclase is often found.

Maximum extinction angles in sections normal to the albite twinning plane range a little under 30 degrees, corresponding to acid labradorite. Analyses of feldspars separated by heavy solution have shown that labradorite containing the soda and lime molecules in about equal proportions is the most abundant plagioclase; but other members of the series, present in considerable amount, range to almost pure albite.

Orthoclase and quartz in graphic intergrowth, as noted above, frequently form a fringe about the plagioclases, and fill many of the triangular and irregular interstices. These

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* In the examination of several hundred sections of Newark diabase from New Jersey and neighboring states only monoclinic pyroxenes have been observed. It seems highly probable that the hypersthene that has been occasionally reported in these rocks is simply pleochroic augite.

areas are sometimes as much as 3 or 4 millimeters across, and are then distinctly visible in the hand specimen, as in the western portion of the Pennsylvania railroad tunnels at Homestead. Frequently individual grains of quartz, and less commonly of orthoclase, are also observed, attaining in some instances a diameter of 1 millimeter.

Magnetite is always present but in greatly varying amount. Crystals are sometimes observed, but most of it, like the augite, is irregularly clustered between the plagioclases, and sometimes partly incloses both the plagioclase and the augite. The frequent presence of magnetite secondary from the alteration of augite renders it impossible in many cases to distinguish with certainty that of primary origin. It is probable that masses molded about the other constituents are largely composed of secondary accretions.

Biotite is also often present in small amount, and is usually clustered about the magnetite in relatively large irregular flakes. It is strongly pleochroic—deep reddish brown and light yellow. Some secondary biotite, after augite, occurs, but in most cases this is readily distinguished from the primary mineral.

Olivine is absent from the great bulk of the rock. It occurs in small amounts, however, near the contacts with the inclosing strata, and is exceptionally abundant in the olivine-diabase ledge of the Palisades, constituting as much as one-fifth of the whole. In the fine-grained border facies of the rock it occurs in scattering porphyritic crystals, which sometimes exhibit resorption phenomena in rounded and embayed outlines. Corrosion mantles or "reaction rims" of radial enstatite occasionally surround the larger crystals, and nest-like aggregates of it entirely replace some of the smaller ones. In this part of the rock mass the olivine is usually more or less altered into yellowish or brownish serpentine; but in the olivine-diabase ledge it occurs in numerous perfectly fresh crystals and irregular grains. Most of it forms poikilitic inclusions in the feldspars and less abundantly in the augites, and it retains a striking freshness and transparency even in the presence of considerable alteration of the augite.

Apatite is always in well-formed prismatic crystals, ranging from very minute up to 1 millimeter in length and 0·06 millimeter in diameter. It is always abundant in the feldspars and quartz, sometimes in plagioclase, sometimes in the quartz-orthoclase intergrowth, and is rarely seen in the other constituents.

Chemical composition.—From a number of analyses that have been made the following are selected to show the range of composition of typical facies of the rock:

Analyses of Palisade Diabase.

	I	II	III	IV
SiO_2	60·05	56·78	51·34	49·02
Al_2O_3	11·88	14·33	12·71	10·14
Fe_2O_3	3·22	5·76	2·65	1·54
FeO	10·21	9·27	14·14	10·46
MgO	0·85	1·58	3·66	17·25
CaO	4·76	5·26	7·44	8·29
Na_2O	4·04	3·43	2·43	1·59
K_2O	2·10	1·75	1·44	0·40
H_2O+	0·66	0·10	0·69	0·59
H_2O-	0·21	0·33	0·18	0·16
TiO_2	1·74	1·44	3·47	0·99
P_2O_5	0·52	0·36	0·20	0·11
MnO	0·28	0·25	0·36	0·16
	100·52	100·64	100·71	100·70

I. Pennslyvania R. R. tunnel, Homestead, 400 feet from the west end.

II. Old quarry near R. R. station, Rocky Hill, 420 feet from upper surface of the trap.

III. Pennslyvania R. R. cut 420 feet east of Marion station (Tonnele Ave.), Jersey City.

IV. Englewood Cliffs, on the Palisades, 11 miles north of Jersey City. From the olivine diabase ledge.

I, III, and IV by R. B. Gage, chemist of the Geological Survey of New Jersey; II by A. H. Phillips of Princeton University (this Journal, vol. viii, 1899, p. 267).

In general, alumina, ferric iron, and the alkalis vary with the silica, while ferrous iron, lime, and magnesia vary inversely. Chemically these rocks overlap the andesite-diorite series on the one hand and the most basic olivine-gabbros on the other, and the extremes are characterized by abundant quartz and olivine, respectively.

Classification.—In the older terminology the prominent facies of the Palisade sill would be known as *quartz-diabase*, *diabase*, and *olivine-diabase*, the prefixes quartz and olivine denoting special richness in these minerals. As indicated above, most of the coarse-grained rock, which constitutes by far the greater bulk of the Palisade sill from the Hudson to the Delaware, is decidedly quartzose, this mineral being quite generally present in graphic intergrowth with orthoclase. In the most acid facies micropegmatite constitutes about one-third of the bulk of the rock, but the average is probably somewhat less than one-tenth. On the other hand, the most basic facies contain 15 to 20 per cent of olivine, but this is confined to the relatively small mass of the olivine-diabase ledge. Normal diabase, without quartz or olivine, is much less abundant than quartz-diabase, and this becomes slightly olivinic near the contacts.

In the quantitative system of Messrs. Cross, Iddings, Pirsson, and Washington the analyses given above would be classified as follows:

- I. Class II. Dosalane
  - Order 4. Quardofelic, Austrare
    - Rang 2. Domalkalic, Dacase
      - Subrang 4, Dosodic, *Dacose*
- II. Class II. Dosalane
  - Order 4. Quardofelic, Austrare
    - Rang 3. Alkalicalcic, Tonalase
      - Subrang 4. Dosodic, *Tonalose*
- III. Class III. Salfemane
  - Order 5. Perfelic, Gallare
    - Rang 3. Alkalicalcic, Camptonase
      - Subrang 4. Dosodic, *Camptonose*
- IV. Class IV. Dofemane
  - Order 1. Perpolic, Hungarare
    - Section 2. Dopyric
      - Rang 1. Permirlic
        - Section 2. Domiric
          - Subrang 2. Domagnesic, *Palisadose*

The great bulk of the rock, judging from about a dozen analyses and a large number of thin sections, appears to be of the type represented by the third of the analyses given above, and might be termed a *graphi-ophito-* to *graphi-grano-camptonose* (III. 5. 3. 4). Notable amounts of the rock, however, belong to the more salic *dacose* (II. 4. 2. 4) and *tonalose* (II. 4. 3. 4) and to the more calcic *auvergnose* (III. 5. 4. 4, 5).

The highly basic ferromagnesian olivine-diabase, of which the fourth analysis above is typical, is a sharply defined facies that may be designated as a *poikili-ophito-* to *poikili-grano-palisadose.* From the typical development of this rock along the Palisades northward from Jersey City it is proposed that the subrang into which it falls (IV. 1^2. 1^2. 2), hitherto unnamed, be designated as *palisadose.*

The relations of these various facies to each other and the problem of their origin are discussed in the report on the petrography of the Newark igneous rocks of New Jersey.* It has already been remarked that the hypothesis of gravitational differentiation seems to account satisfactorily for all the conditions observed.

Composition of the Augite.—Analyses of the augite from this sill at Rocky Hill† and from the very similar intrusive at West Rock, New Haven, Conn.,‡ yielded the following results:

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* Annual Report of the State Geologist of New Jersey for 1907.

† A. H. Phillips, loc. cit.

‡ G. H. Hawes, this Journal, vol. ix, p. 185, 1875.

Analyses of Augite from the Palisade Diabase.

	I.	II.	III.	IV.
SiO_2	47·72	48·54	50·71	47·10
Al_2O_3	3·44	5·50	3·55	4·55
Fe_2O_3	5·93	2·77	n. d.	n. d.
FeO	18·34	21·25	15·30	15·20
MgO	12·89	7·67	13·63	18·65
CaO	11·40	10·97	13·35	11·33
Na_2O	0·86			
		3·10	1·48[1]	n. d.
K_2O	0·37			
MnO	n. d.	n. d.	0·81	0·17
Ign.	0·00	0·82	1·17	1·33
Insol.	----	----	----	0·34
	100·95	100·62	100·00	98·67

[1] By difference.

I. Rocky Hill, N. J. Quarry near the middle of the trap sheet. A H. Phillips, analyst.

II. Rocky Hill, N. J. Old quarry near the railroad station, about 420 feet from the upper contact. A. H. Phillips, analyst.

III. West Rock, New Haven, Conn. G. W. Hawes, analyst.

IV. Aakeroe, Sweden. Partial analysis of diallage by H. von Post. *

With the exception of small deficiencies in silica in I, II, and IV, these analyses correspond to the following pyroxene molecules in the proportions indicated:

Acmite, $NaFe(SiO_3)_2$ = ac.
Hypersthene, $(Mg,Fe)SiO_3$ = hy.
Diopside, $Ca(Mg,Fe)(SiO_3)_2$ = di.
Aluminous molecule, $(Mg,Fe)(Al,Fe)_2SiO_6$ = alm.

	ac.	hy.	di.	alm.	
I.	108	640	816	159	=
	1	5·93	7·56	1·47	=
	2	12	15	3	(approx.)
II.	270	530	784	81	=
	3·33	6·54	9·68	1	=
	7	13	19	2	(approx.)
III.	126	522	956	69	=
	1·83	7·72	13·86	1	=
	2	8	15	1	(approx.)
IV.	?†	864	808	135	=
		6·40	5·99	1	=
		13	12	2	(approx.)

These formulas indicate a quite exceptional composition for augite in the great excess of ferrous iron and magnesia over lime, alumina, and ferric iron.

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* Dana's System of Mineralogy, 6th ed., p. 360.

† Ferric iron and alkalis not determined.

Composition of the Feldspars.—Feldspars were also separated and analyzed from the Rocky Hill material by Phillips and from the West Rock locality by Hawes. Omitting non-feldspathic constituents and assigning the potash to orthoclase, and the soda and lime to albite and anorthite, respectively, the analyses show the following constitution :

Mineral Constitution of the Feldspars.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Sp. gr.	$>2{\cdot}69$	$<2{\cdot}69$	$>2{\cdot}69$	$<2{\cdot}69$	$<2{\cdot}60$	$=2{\cdot}577$	$>2{\cdot}69$	$<2{\cdot}69$
Orthoclase	7·5	7·7	13·2	12·6	27·4	31·7	6·0	7·2
Albite	47·1	71·3	60·6	70·3	68·9	64·2	24·4	40·9
Anorthite	45·4	21·0	26·2	17·1	3·7	4·1	69·6	51·9
	ab_1an_1	ab_7an_2	ab_5an_2	ab_9an_2	$ab_{20}an_1$	$ab_{17}an_1$	ab_3an_8	ab_5an_6

I, II. Rocky Hill. Quarry near the middle of the trap sheet.

III, IV, V, VI. Rocky Hill, N. J. Old quarry near upper contact.

VII, VIII. New Haven, Conn. West Rock.

The plagioclase molecules as calculated range from nearly pure albite to labradorite. It is probable, however, that some of the soda is combined with the potash in orthoclase and anorthoclase. On the other hand, it is also quite possible that small amounts of more basic plagioclases would have been found if the heaviest portions had been further separated before analysis. The frequent occurrence of zonal structure in the plagioclases, however, seems to indicate that these minerals do not occur in individualized grains of uniform composition, but have been built up into composite crystals of successively more acidic and more sodic character. In the instances determined the portion with the highest specific gravity constituted more than half the total feldspars, so that the labradorite molecule undoubtedly predominates.

Metamorphic effects.—Contact metamorphism has produced an elaborate series of hornfels, rocks characterized by various combinations of feldspar, biotite, quartz, augite, hornblende, tremolite, garnet, spinel, magnetite, muscovite, cordierite, scapolite, vesuvianite, sillimanite, andalusite, chlorite, calcite, analcite, titanite, tourmaline, zircon, apatite, and possibly leucite. The various types within the zone of metamorphism seem to vary with the original composition of the shales, and not to depend on relative distances from the contact nor degree of metamorphism.

Metamorphic arkose, both in the inclusions and at the contacts, contains besides the usual plagioclase, orthoclase, and some quartz, also augite, biotite, epidote, cordierite, chlorite, calcite, tourmaline, and apatite.

The contact metamorphic effects of the sill at Hoboken, New Jersey, have been described by Andreae and Osann,* who show that it is of exomorphic pneumatolytic character. To the four types of hornfels which they describe, J. D. Irving† has added five others, and the present studies, in which no attempt has been made to present a complete series of alteration products, have brought out eight additional types of hornfels and four of metamorphic arkose. These might be extended almost indefinitely, since they do not occur as sharply defined types, but present various degrees of gradation from one to another. Furthermore, they do not form zones or belts in any systematic order with relation to the intrusive rock, but alternate irregularly throughout all parts of the zone of metamorphism. It is evident, therefore, that the types observed are not the results of varying degrees of metamorphism, but are dependent only on original variations in the composition of the shales and sandstones themselves.‡

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* Andreae and Osann, Tiefen contacte an intrusiven Diabasen von New Jersey; Verh. d. Naturh. Med. Ver. zu Heidelberg. N. F. V., Bd. I, 1892.

† School of Mines Quarterly, vol. xx, pp. 213–223, 1899.

‡ For descriptions of these rocks, and of other igneous rocks besides the great intrusive sill, see "Petrography of the Newark Igneous Rocks of New Jersey," Ann. Report of the State Geologist of New Jersey for 1907, pp. 98–169.

Art. XX.—*A New Horse from the Lower Miocene;* by F. B. Loomis.

While the series of fossils, which show us the development and radial adaptations of the horse family, is already a large one, there still remain breaks and places where more material is desired. Such an unfilled gap exists between the rich Oligocene Mesohippus fauna and the upper Miocene Protohippus group, just where the transition from the brachydont uncemented teeth to the hypsodont cemented ones occurs. The finding by Peterson* of the excellent type of Parahippus nebraskensis in the Upper Harrison beds of Nebraska, closed in a part of this gap, and for two or three seasons fragments have raised the expectation of a Lower Harrison horse. During the season of 1907, under the guidance of Mr. Harold Cook, the Amherst '96 expedition found a prospect, which proved to be the major part of the skull of this much desired type. While the brain case is wanting, a nearly perfect upper and lower dentition of an adult individual is preserved, showing an animal closely related to *P. nebraskensis*, but about a fourth smaller. The following specific description will point out the affinities and characters of the new species.

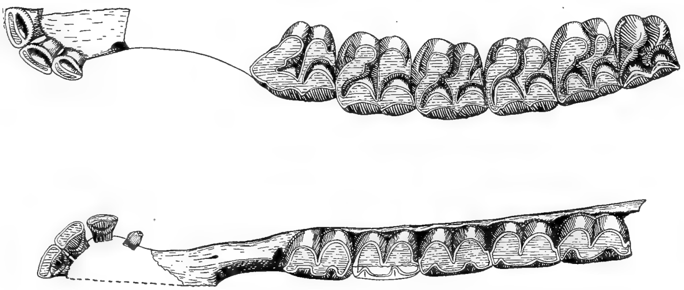

Fig. 1.—Crown views of the upper and lower dentition of the type of Parahippus tyleri. One-half natural size.

Parahippus tyleri sp. nov.

Type, a skull numbered 1079 in the Amherst College Museum, which while lacking the brain case preserves all the dentition except the upper canine and the first premolar of the

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* Ann. Carnegie Museum, vol. iv, p. 57, 1906.

upper and lower jaw. The specimen was found in the upper part of the Lower Harrison beds, 8 miles northeast of Agate, Sioux Co., Nebraska; and is named to honor Prof. J. M. Tyler, the organizer of the Amherst expeditions.

While having a rather short facial portion, the skull is moderately high and narrow. The individual being described is an adult, only recently matured, as indicated by the moderate wear on the teeth and the fact that the third upper molar is scarcely worn at all. On the upper incisors the pit is deep, being entirely surrounded on the inner side by the raised cingulum. This pit seems to be more developed than in *P. nebraskensis.* A canine is indicated by a small alveolus a short distance from the third incisor. The first premolar is wanting in this specimen. The second to the fourth premolars, while slightly larger, grade into the molars having the same characteristics. While the parastyle and the mesostyle are well developed they are not as prominent as in *P. nebraskensis.* A remnant only of the cingulum is present on the inner part of the front border of each tooth. The protocone and protoconule unite to make a strong protoloph, but are separated from each other by a narrow constriction. On the metaloph of premolar four and the succeeding molars a small crochet is developed, which while distinct does not however unite with any part of the protoloph; consequently the prefossette is not entirely isolated. The hypostyle is strong and notched in the rear.

On the lower jaw the pit in the incisors is not as well developed as in incisors of the upper jaw, appearing more like a groove behind a well-marked cingulum. The lower canine is a simple cone of moderate size. The first premolar is indicated by a small alveolus and must have been tiny. The remaining premolars and molars each have a well-marked cingulum, starting from the parastylid, continuing around the outer border, and back to a tiny hypostylid. The inner wall of each tooth is relatively straight, the upper part being, in little worn teeth, notched to separate off the strong parastylid, and again between the paraconid and hypoconid. The heel of the third molar is moderate in size and simple in form.

While very like, and probably ancestral to *P. nebraskensis*, this species is distinguished by the less pronounced parastyle and mesostyle, by the relatively narrower teeth, the deeper pit in the incisors, and the smaller size. It is a primitive member of the genus, the crochet not uniting with the protoloph and cement being entirely absent.

Measurements.

Length of the upper incisor series	28^{mm}
Distance from incisor 3 to the canine	11
Length of the upper premolar series	59
Length of upper premolar 3	20
Width of upper premolar 3	25
Length of the upper molar series	55
Length of upper molar 2	19
Width of upper molar 2	26
Length of the lower premolar series	56
Length of the lower molar series	59
Width of lower molar 1	14

Amherst College, Department Biology,
May 29, 1908.

SCIENTIFIC INTELLIGENCE.

I. Geology.

1. *Indisches Perm. und die permische Eiszeit;* by E. Koken. N. Jahrb. f. Min., Festband 1907, pp. 446–546, and a large paleogeographic map.—This is a very important paper to all students of Permian and Triassic stratigraphy and to glaciologists. Noetling has in Koken a strong supporter for his Indian Permian stratigraphic correlations. The broader views of equivalency put forth some years ago by Tschernyschew are rejected. Koken holds that the Productus limestone of India passes without break into the Triassic, as it also does in the eastern Alps where the Bellerophon beds pass into the Werfen. Beneath the Productus limestone occur the Permian glacial deposits, the material having come from the south or peninsular India. Sands of glacial origin are also seen in the higher limestone and even in the Triassic—the regolith of the southern lands carried by the rivers into Tethys.

Various theories in regard to the probable causes for the Permian glaciation are discussed at length and Koken rejects the carbon dioxide theory of Arrhenius, and, as well, that of the wandering of the pole. He concludes that the probable cause is to be looked for rather in changed relations of the continents to equatorial waters, and therefore in the changed streaming of oceanic currents. During Permian glaciation India stood high and Australia was united to India and Africa, deflecting the southern equatorial waters away from the Indian Ocean and the Antarctic region. The melting of the Permian ice was due to the isolation of Australia from India, as along nearly all of the west coast of the former land are found Permian deposits. This opening again permitted the southern equatorial currents to stream into the Indian Ocean. Koken's generalizations have added value because of his detailed paleontologic knowledge. C. S.

2. *Geological Survey of Western Australia, Bulletin 29. A Report upon the Geology, together with a Description of the Productive Mines of the Cue and Day Dawn Districts, Murchison Goldfield;* by HARRY P. WOODWARD, Assistant Government Geologist. Part I, *Cue and Cuddingwarra Centres;* pp. 93, with 3 maps, 12 photographs, 2 blocks, and 15 plates of sections. Part II, *Day Dawn Centres;* pp. 43 and appendices, pp. 44–53, with 2 maps, 7 photographs, 1 figure, and 8 plates of sections. Perth, 1907.—The general conditions under which gold deposits occur in Murchison are in lenticular-shaped amphibolite belts, "surrounded or sandwiched with granites, the whole being intersected by numerous feldspathic dikes." The oldest rock of the Cuddingwarra and Day Dawn districts is an amphibolite. Grano-diorite occurs as a magmatic intrusion into the amphibolite. A remnant flow of vesicular andesite caps Cue hill. The topography is diversified by the presence of "table tops" made of granite "which owes its weather-resisting character to iron oxide which has been drawn up in solution by capillary attraction through leaching of the rocks below".

Gold occurs chiefly in quartz reefs, the production being—Cue, 212,855 ounces, Cuddingwarra, 35,461 ounces, and Day Dawn, 847,692 ounces. H. E. G.

3. *Illinois State Geological Survey,* H. FOSTER BAIN, Director. Bulletin No 7. *Physical Geography of the Evanston-Waukegan Region;* by WALLACE W. ATWOOD and JAMES W. GOLDTHWAIT. Pp. 93, pls. 14, figs. 52. Urbana, 1908.—It is becoming recognized that geologists are under obligation to present the main facts of their science in such a manner as to be of direct use to teachers and to the general reader. Following the lead of the Connecticut Survey, the Geological Survey of Illinois has planned a series of bulletins dealing with the physical geography of the state and designed primarily to present material more or less well known to experts in a form directly available for the intelligent reader. The volume in the series listed above is well arranged, well written and illustrated and contains interesting material. H. E. G.

4. *Map of Vesuvius.*—The *Instituto geografico militare* of Italy, at Florence, has published a new edition (1908) of an excellent map of Vesuvius in colors, on a scale of 1 : 25,000 (2 francs) indicating all determinable lava flows, with their dates, down to 1906; also a map of the volcano in black, in six sheets, scale 1 : 10,000 (4.50 francs for the set); also two special maps of the cone of the volcano, 1 : 10,000, before and after the eruption of 1906 (each, one franc). Of the general map of Italy, 1 : 100,000, by far the most legible edition is the one known as "*systema Gliamas,*" in four colors, now in course of publication (1.50 francs a sheet, 27 sheets published; edition on thin paper preferable). W. M. D.

5. *A Pocket Handbook of Minerals, designed for use in the field or class-room, with little reference to Chemical Tests;* by G. MONTAGUE BUTLER. Pp. ix, 298 with 89 figures and 5 tables. New York, 1908 (J. Wiley & Sons).—Mineralogists and others who feel the need of a small volume suitable for the pocket, giving the important characters of the prominent mineral species, will find this work suited to their needs. It is printed in particularly clear, open form, with the emphasis upon essential characters and the omission of unnecessary detail; there are numerous illustrations. A novel feature is the series of tables at the end presenting the characters of the species in condensed form.

II. BOTANY.

1. *The Origin of a Land Flora; a Theory based upon the Facts of Alternation;* by F. O. BOWER, Regius Professor of Botany in the University of Glasgow. Pp. xi + 727, with frontispiece and 361 text-figures. London, 1908 (Macmillan & Co.).—Professor Bower has long been recognized as one of the ablest authorities on the morphology of the Pteridophytes, a group of plants to which the present work is largely devoted. He clearly shows that representatives of this group were the first plants to solve successfully the problems of terrestrial life, and that the Phanerogams, or seed-bearing plants, which are now in the ascendant, were derived from the Pteridophytes by further specialization. The evidence for these opinions is drawn almost entirely from the sporophyte, or asexual generation, the lines of gametophytic development in land plants reaching their culmination in certain divisions of the Bryophytes. The great gap which exists between the bryophytic sporophyte with its continuous spore-cavity and lack of lateral organs and the pteridophytic sporophyte with its distinct sporangia and well developed leaves is still unfilled, but three main factors of advance are indicated, namely: sterilization of originally fertile cells; segregation of sporogenous tissue into distinct masses; formation of roots and of appendicular organs, such as leaves, on the axis or stem. The fact is also emphasized that the primary function of the sporophyte is, after all, the production of spores, so that, in the evolution of the Pteridophytes, the sporophyll was probably the first type of leaf to appear, the true foliage leaf arising from the sporophyll by further sterilization. On the basis of these views the author advances the idea that the sporophyte in the original Pteridophytes consisted of an axis attached to the soil by a root-system and bearing a cluster of small sporophylls, each with a single sporangium. The closest approach to this condition is apparently to be seen in such a plant as Lycopodium Selago, where the sporophylls are indefinite in position and essentially like the small foliage leaves in appearance and structure. The large and frequently compound leaves which are characteristic of the Filices and Ophioglossales have apparently been derived from small and simple leaves by longer continuance of growth and increase in complexity. Professor Bower designates the theory

which he defends as the theory of the "strobilus," or "strobiloid" theory. He admits that the theory is hardly capable of direct proof and claims no originality for certain of the views advanced, but the evidence which he presents is clear and usually convincing. The strobiloid theory, in which the axis is the part originally dominant, is in marked contrast to certain theories proposed by earlier writers, in which the leaf either precedes the axis or is simultaneous with it in its appearance. A. W. E.

2. *Linnaeus;* by Dr. VALCKENIER SURINGAR; pp. 106. S. Gravenhage, 1908 (Martinus Nijhoff).—The author gives an account of the more important works published by Linnaeus with an estimate of their value and indicates the influence which they exerted upon later writers. In the course of the treatise he calls attention to certain passages, some of them now almost forgotten, which contain the germs of some of the theories which have played an important part in the subsequent development of biological science. A. W. E.

3. *Die Algenflora der Danziger Bucht; ein Beitrag zur Kenntniss der Ostseeflora;* by Prof. Dr. LAKOWITZ, Oberlehrer am königlichen Gymnasium in Danzig. Pp. vii+141, with 70 text-figures, 5 double plates, and a map. Danzig, 1907 (published by the Westpreussischer Botanisch-Zoologischer Verein).—The present work represents an important contribution to our knowledge of the algal flora of the Baltic Sea. In the first section the numerous species occurring in the Danzig Bay are fully described and figured and artificial keys are provided for the determination of the genera. In the second section the flora is described from an ecological standpoint, and the distribution of the various species represented is discussed. The five double plates give photographic reproductions of the larger algae in natural size and the text-figures show microscopic details.

A. W. E.

4. *A Text-Book of Botany;* by Professors STRASBURGER, NOLL, SCHENCK and KARSTEN; third English edition revised with the eighth German edition by Dr. W. H. LANG; pp. x+748, with 779 illustrations, in part colored. London, 1908 (Macmillan & Co.).—The Bonn Text-Book of Botany has now reached its ninth German edition, the first one having appeared in 1895. The demand for so many editions within so short a time gives an indication of its great popularity, and it is without doubt the most comprehensive and satisfactory botanical text of the present time. When the third English edition is compared with the second, which was published in 1898, the most important changes are to be found in the section devoted to the Phanerogamia. This portion of the work was originally prepared by Professor A. F. W. Schimper, but upon his death was entirely rewritten by Professor Karsten. Schimper's treatment still appears in the second English edition, but is replaced by Karsten's in the third. The three other sections of the book, devoted respectively to Morphology, Physiology, and the Cryptogams, are brought down to date, and a copious index of literature concludes the volume.

A. W. E.

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SCIENTIFIC INTELLIGENCE.

Dr. Cyrus Adler,
Librarian U. S. Nat. Museum.

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[FOURTH SERIES.]

ART. XXI.—*On the Retardation of "Alpha Rays" by Metal Foils, and its Variation with the Speed of the Alpha Particles*; by T. SMITH TAYLOR.

[Contributions from the Sloane Laboratory of Yale College.]

Introduction.

IN 1905, Bragg and Kleeman* observed that the α-ray ionization curve, obtained with a metal sheet over the source of the rays (radium), did not suffer the same drop from the normal curve at all points. The portion of the curve corresponding to radium C suffered a greater drop than that due to radium itself. The loss of range of the α particle of radium C in passing through the sheet of metal was thus greater than the loss of range of the α particle from radium in passing through the same sheet. This seemed to be evidence that the slower α particles from radium were a little less affected by their passage through the sheet than the swifter α particles from radium C.

Kucera and Masek† measured the amount by which the range of the α particles from radiotellurium (polonium) was cut down by their passage through a sheet of aluminium and a sheet of platinum. They measured this diminution in range produced by the aluminium and the platinum when the sheet was directly over the radiotellurium and when the sheet was $1{\cdot}9^{\mathrm{cm}}$ from it. They found the diminution produced in the latter case to be less, by 10 per cent for the aluminium and 12·5 per cent for the platinum, than in the former case. They also describe experiments from which one can conclude that the range lost by an α particle in going through two sheets of dissimilar metals is independent of the order in which it passes through them. This appears to be inconsistent with the previous statement.

Experiments made by McClung,‡ Rutherford§ and Levin‖ are also inconsistent with Bragg's results as well as with the

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* Phil. Mag., Sept. 1905.

† Phys. Zeitschr., xix, pp. 630–40, 1906.

‡ Phil. Mag., Jan. 1906.

§ Phil. Mag., Aug. 1906.

‖ Phys. Zeitschr., xv, 519–521, 1906.

first statement of Kucera and Masek above. Rutherford found that the a particle loses energy at a uniform rate during its passage through aluminium. McClung, Levin, and Kucera and Masek* obtained results indicating that each successive layer of aluminium foil which is laid upon a radioactive substance diminishes the range of the a particle by an equal amount.

On the other hand, Bragg† observed that the stopping power is not independent of the speed as stated by Rutherford, McClung and Levin; Bragg found that the ionization curve, obtained when a sheet of gold foil was directly above the radium C, suffered a greater drop than when the sheet was at a distance of $1{\cdot}5^{\text{cm}}$ from it. The range of the a particle when two metals, Al and Au, were placed over the radium, was not independent of the order in which they were arranged. The range was diminished by a greater amount when the gold foil was next to the radium and the aluminium over it than when the order was reversed. Similar results were obtained for aluminium and tin when their order was reversed as in the above case. Meyer‡ also observed this same effect.

Kucera and Masek,§ and Meitner,‖ ascribe these latter effects, as they observed them, to a difference in the amount of the scattering of the rays by the two metals. Their argument as presented does not seem to be conclusive; for the scattering, if it exists, is a differential effect.

In all the experiments cited, the method of obtaining the air equivalents¶ corresponding to different positions of the screen has been to measure the range with the source uncovered and then with the screen in place. The difference of these values gives the air equivalent of the sheet.

As, however, the variations in the air equivalent are small, this is not a very accurate or sensitive method; since the air equivalent itself (whose small variations are to be observed) is obtained as the difference between two much larger quantities (the ranges) neither of which can be determined with great accuracy. A method of observing the *variations* of the air equivalent was sought which should be free from these disadvantages.

Description of Apparatus.

The apparatus, as shown in figures 1 and 2, was similar to that used by Bragg. The ionization chamber, which was 5^{cm} in diameter and 2^{mm} in depth, was formed by the wire gauze,

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* Loc. cit.

† Phil. Mag., April, 1907.

‡ Phys. Zeitschr., xiii, 425, July, 1907.

§ Ibid. vii, 19, 1906.

‖ Ibid. viii, 489, 1907.

¶ By air-equivalent is meant the diminution in the range of the a particle produced by the foil when placed over the source of rays, or the amount by which the range of the a particles in air is cut down by their passage through the foil.

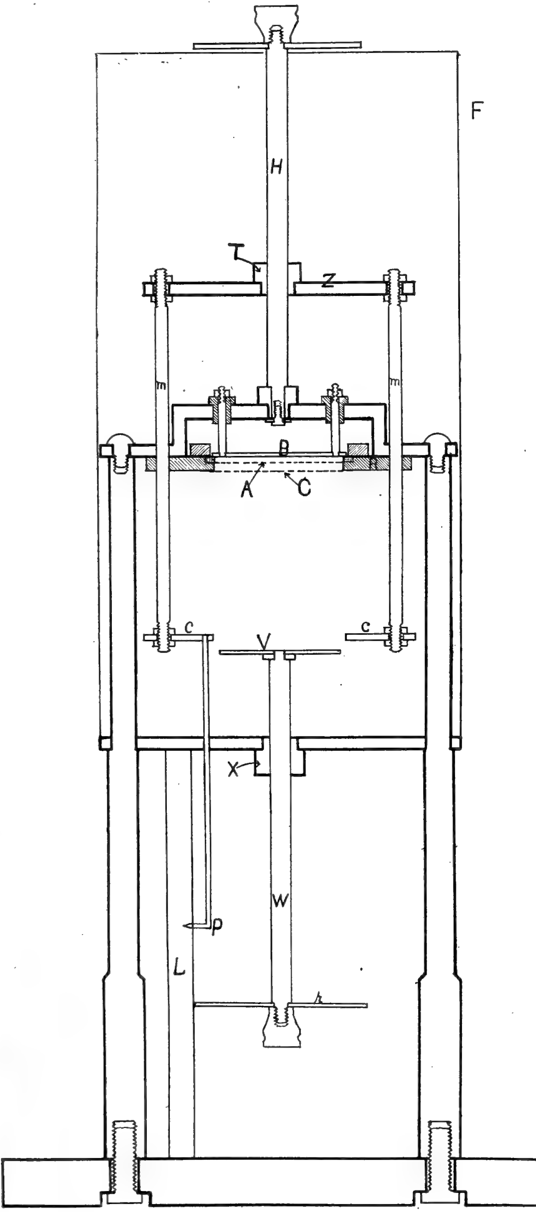

FIG. 1.

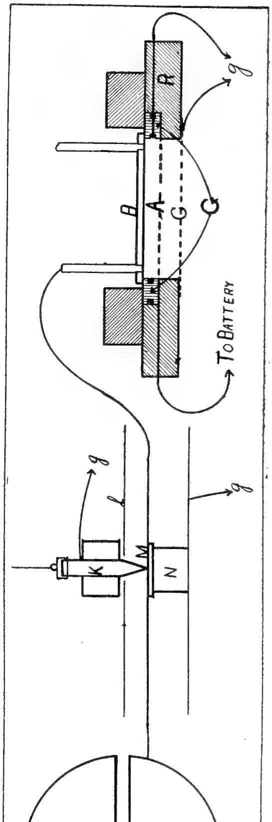

FIG. 2.

A, and the brass plate, B. The gauze A was carefully insulated from the plate B by means of an ebonite ring G. To prevent any possible leakage from A to B a fine copper wire was run in a groove around the inner edge of this ring, then through the ring and around its outer edge, and, after passing through the large ring of ebonite R, to the earth. A second gauze C was placed 3^{mm} below A and, being earthed, formed with it a second ionization chamber which prevented stray ions from entering the main chamber.

The plate B was connected to one pair of quadrants of a Dolezalek electrometer as shown in figure 2, the second pair of quadrants being earthed. K is a key by means of which the one pair of quadrants and plate B could be earthed or insulated at pleasure. K rested on a brass plate M, which in turn was insulated from the protecting case *l* by being placed upon a block of sealing wax N.

The polonium, which was used as the source of rays, being put upon the plate V, could be moved towards or from the ionization chamber by means of the screw W, of 1^{mm} pitch, working in the nut X. Its distance from the chamber could be determined by the scale L and the graduated circular disc *r*. The metal sheets were placed upon the brass ring *c*, *c* and could be moved to different positions by means of the screw H, of 1^{mm} pitch, working in the nut T. The distance of the metal sheet from the polonium could be read from the scale L by means of the pointer P, which extended below the case F from the moveable framework *cm*Z.

The polonium kindly prepared for me by Prof. Boltwood was deposited upon the end of a copper plug, which could be fitted into a block of brass and adjusted to a definite distance from the top of the block. The opening in the block above the polonium was 4^{mm} in diameter and 6^{mm} high. This limited the cone of rays given off by the polonium so that all the rays would fall within the ionization chamber.

The ebonite was carefully polished to prevent leakage over its surface. The entire framework of the apparatus together with the tin case F and the protecting case *l* for the connection of the plate B to the electrometer was grounded. Care was taken to avoid all outside electrostatic effects upon the electrometer as well.

Method of Experiments.

The block containing the polonium was put upon the disc V and a metal sheet on the ring *c*, *c*, which was then adjusted by means of the screw H until the sheet just touched the top of the block, thus being 6^{mm} from the polonium. With a constant potential of -40 volts on the gauze A and the metal sheet at a distance of 6^{mm} from the polonium, the Bragg ionization curve was plotted.

In figure 3, curves I and II represent parts of the top portion of two Bragg curves* as obtained when a sheet of gold foil was kept at a distance of 6^{mm} from the polonium. Curve I was plotted from readings taken at the end of the first minute and curve II from readings taken at the end of the second minute. The curves being plotted with magnified ordinates have much greater slopes than they would have if plotted on the ordinary scale.

The polonium, with the gold foil 6^{mm} above it, was then set at a distance of $3{\cdot}0^{cm}$ from the ionization chamber. As can be seen from curves I and II, this distance was such that the deflections obtained corresponded to two points in the slightly inclined (top) portions of the Bragg curves. With the polonium at this distance of $3{\cdot}0^{cm}$ from the ionization chamber, the gold foil was moved away from the polonium towards the ionization chamber, and the ionization was measured when the sheet was at various distances from the polonium. It was found that the ionization increased as the distance of the gold sheet from the polonium increased.

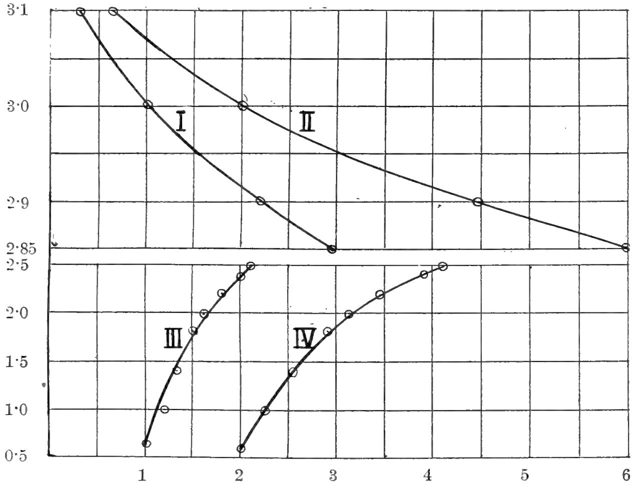

FIG. 3. The ordinates of curves I and II are the distances in centimeters of the polonium from the ionization chamber. The ordinates of III and IV are the distances in centimeters of the sheet of gold from the polonium when the polonium was kept at a distance of $3{\cdot}0^{cms}$ from the ionization chamber. The abscissas of I and III are the deflections in centimeters of the electrometer needle at the end of the first minute, and the abscissas of II and IV are the deflections at the end of the second minute.

In figure 3, curves III and IV were plotted with the deflections of the electrometer needle at the end of the first and second minutes respectively as abscissas, and with the distances

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* This is the portion of the ionization curve which, as ordinarily plotted, is nearly horizontal.

of the sheet of gold from the polonium, corresponding to these deflections as ordinates (the polonium being kept at a distance of 3·0^{cm} from the ionization chamber). Curves similar to III and IV in figure 3 were also plotted for the gold foil when the polonium was set at distances other than 03·^{cm} from the ionization chamber. The distance of the polonium from the ionization chamber was always so chosen that the chamber cut the Bragg curve somewhere in the slightly inclined portion. The Bragg curves I and II were determined each time before making the measurements plotted in curves III and IV for any given distance between the polonium and the ionization chamber. In this way, several sets of curves similar to the ones in figure 3 were obtained for each metal sheet given in Table II.

The diminution in the range of the a particle produced by the sheet when 6^{mm} from the polonium (its air equivalent in this position) was determined by first plotting the ionization curve without the sheet over the polonium and then with the sheet over it. The difference between the ordinates of the two curves corresponding to a given abscissa, which was the deflection of the electrometer needle, was the diminution in range of the a particle produced by the sheet, or what is the same, its air equivalent. This is the same as taking the deflection of the needle without the sheet over the polonium when it is at a certain distance from the chamber, and, after placing the sheet over the polonium, noting how far the polonium and sheet must be moved towards the ionization chamber to get the same deflection of the needle.

Determination of the Variation in the Air Equivalents.

As previously stated, when the polonium, with a metal sheet 6^{mm} above it, was set at such a distance from the ionization chamber that the chamber cut some part of the slightly inclined portion of the Bragg curve, it was found that, by moving the sheet farther away from the polonium, the ionization increased as the distance of the sheet from the polonium increased. This signifies that by moving the sheet away from the polonium the entire ionization curve was pushed upward, so that the part of the slightly inclined portion, which fell just below the ionization chamber when the sheet was 6^{mm} from the polonium, fell within the chamber when the sheet was at a little greater distance from the polonium.

This means that the total range of the a particles is greater with the sheet at the greater distance from the polonium ; and the magnitude of this increase in total range (which is also the diminution in the air equivalent of the sheet) can be obtained directly from the measured ionizations, given in curves III and IV, and the curves I and II, fig. 3.

The diminution in the range produced by a given sheet when $0{\cdot}6^{cm}$ from the polonium, having been determined by the direct method as previously stated, the diminution at any other distance was found from the curves in figure 3, which were plotted on finely ruled co-ordinate paper, thus facilitating the determination. The curves given in figure 3 were for a sheet of gold (A in Table II), which cut down the range $0{\cdot}635^{cm}$ when it was $0{\cdot}6^{cm}$ from the polonium.

The method of making the determination can be illustrated by finding the diminution in range produced by the sheet when it was at a distance of $1{\cdot}8^{cm}$ from the polonium. In curve III the abscissa, corresponding to the ordinate 1·8, which is the distance of the sheet from the polonium, is seen to be 1·5. The abscissa 1·5 in curve I corresponds to the ordinate 2·956 in the same curve. Thus the increase in the deflection of the electrometer needle produced when the sheet is moved from $0{\cdot}6^{cm}$ to $1{\cdot}8^{cm}$ from the polonium is the same as would be produced if the polonium with the sheet 6^{mm} above it were moved from $3{\cdot}0^{cm}$ to $2{\cdot}956^{cm}$ from the ionization chamber. The total range of the *a* particles when the sheet is $1{\cdot}8^{cm}$ from the polonium, is greater by $[3{\cdot}0-2{\cdot}956]$ $0{\cdot}044^{cm}$ than the total range when the sheet is $0{\cdot}6^{cm}$ from the polonium. In a similar manner we find from curves IV and II this change is equal to $0{\cdot}042^{cm}$. The mean value for the two determinations is then $0{\cdot}043^{cm}$. The barometer stood at $760{\cdot}2^{mm}$ when the curves were plotted, and hence this change of the range when reduced to barometer 760^{mm} is

$$\frac{760{\cdot}2 \times 0{\cdot}043}{760} = 0{\cdot}043^{cm}$$

Since there is this difference in the total range of the *a* particles in the two cases, it is evident that the sheet does not cut down the range of the *a* particles as much when it is $1{\cdot}8^{cm}$ from the polonium as when it is only $0{\cdot}6^{cm}$ from the polonium, and that the air equivalent of the sheet at $1{\cdot}8^{cm}$ distance from the polonium is $0{\cdot}043^{cm}$ less than at $0{\cdot}6^{cm}$.

In this manner the air equivalent of the sheet was found when it was at various distances from the polonium. In Table I are given the values of these air equivalents for the A sheet of gold corresponding to the distance of the sheet from the polonium and the range that the *a* particle still had in air at atmospheric pressure when it entered the sheet. The range of the *a* particle in air at atmospheric pressure was found to be $3{\cdot}77^{cm}$. This was the distance from the polonium to the upper side of the gauze A when the ionization, due to the *a* particles from the polonium, produced the first noticeable deflection of the electrometer needle above that due to the spontaneous ionization of the air in the chamber.* The spontaneous

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* If the distance had been measured to the middle of the ionization chamber the range would be $3{\cdot}87^{cm}$, which is the value usually taken.

ionization of the air in the chamber produced less than 0·04$^{\text{cm}}$ deflection. This is so small as to be practicably negligible. But had it been larger it would have made no difference; because it would have the effect of shifting all the curves in figure 3 to the right by an equal amount, thus not changing their relative positions or forms.

Column 1 in Table I contains the distance in centimeters of the sheet from the polonium. Column 2 gives the range in centimeters of the *a* particle when entering the sheet. In column 3 are given the air equivalents in centimeters of the sheet corresponding to the distances in column 1 and the ranges in column 2 as determined when the polonium was set at 3·1$^{\text{cm}}$ from the ionization chamber. Columns 4, 5, 6, 7 and 8 contain the same quantities as column 3, as determined with the polonium at 2·9, 3·0, 3·1, 2·8 and 3·0$^{\text{cm}}$ respectively from the chamber.

TABLE I. A Au.

Distance from polonium to the sheet	Range of entering particle	3·1	2·9	3·0	3·1	2·8	3·0	Means.
0·6	3·17	0·635	0·635	0·635	0·635	0·635	0·635	0·635
0·8	2·97	0·626	0·628	0·629	0·626	0·629	0·630	0·628
1·0	2·77	0·619	0·620	0·622	0·618	0·621	0·623	0·621
1·2	2·57	0·613	0·614	0·616	0·611	0·613	0·616	0·614
1·4	2·37	0·606	0·609	0·608	0·603	0·605	0·609	0·607
1·6	2·17	0·600	0·601	0·600	0·596	0·595	0·601	0·599
1·8	1·97	0·592	0·595	0·592	0·589	0·584	0·592	0·591
2·0	1·77	0·582	0·581	0·582	0·579	0·574	0·581	0·580
2·2	1·57	0·572	0·567	0·571	0·569	0·564	0·570	0·569
2·4	1·37	0·556	0·548	0·555	0·556	0·557	0·552	0·553

The last column contains the average values of the six preceding columns. The agreement between corresponding quan-

TABLE II.

I Metal sheets	II Thickness in cms.	III Air equiv. in cms.	IV Ratio
A Au	0·000127	0·635	4·99 × 10^{3}
B Au	0·000174	0·857	4·91 × 10^{3}
A Pb	0·000284	0·923	3·24 × 10^{3}
B Pb	0·000411	1·231	3·01 × 10^{3}
A Sn	0·000386	0·886	2·29 × 10^{3}
B Sn	0·000799	1·800	2·25 × 10^{3}
A Al	0·00033	0·574	1·74 × 10^{3}
B Al	0·000612	1·04	1·70 × 10^{3}
A Ag	0·000223	0·676	3·03 × 10^{3}

tities in these columns shows that possible errors in plotting the Bragg curves (e. g., I and II in figure 3) produced no errors of importance in the reduction.

In this manner, the air equivalent of the metal sheets given in Table II were determined for the various distances of the sheets from the polonium. The values obtained are found in Table III.

TABLE III.

Range in cms. of entering particle.	A Au	B Au	A Pb	B Pb	A Sn	B Sn	A Al	B Al	A Ag
3·17	0·635	0·857	0·923	1·231	0·886	1·800	0·574	1·040	0·676
2·97	0·628	0·849	0·914	1·220	0·879	1·787	0·574	1·029	0·673
2·77	0·621	0·839	0·903	1·207	0·871	1·768	0·573	1·017	0·669
2·57	0·614	0·828	0·891	1·193	0·862	1·744	0·572	1·005	0·664
2·37	0·607	0·816	0·878	1·178	0·852	1·718	0·571	0·990	0·659
2·17	0·599	0·801	0·861	1·160	0·840		0·568	0·970	0·652
1·97	0·591	0·783	0·843	1·138	0·827		0·563	0·949	0·644
1·77	0·580	0·761	0·819		0·810		0·555		0·635
1·57	0·569	0·735			0·797		0·544		0·625
1·37	0·553						0·532		0·613

The values of the air equivalents for each of the metal sheets recorded in Table III represent the results obtained from a series of determinations similar to that given for A Au in Table I. The agreement in the values, obtained for the different positions of the polonium, was equally as good as that for the A Au. These separate tables for each metal sheet have been omitted for the sake of brevity and only the average results given in Table III.

The curves in figure 4 represent the results as recorded in Table III. By noting the slope of these curves, one can obtain some comparison of the rate at which the air equivalents of the various sheets are changing. For the thinner sheet of Al, the air equivalent is almost constant for the higher ranges, but, as the range of the entering a particle decreases, the air equivalent decreases slowly and, in the lower ranges the decrease becomes quite marked. The thicker Al, however, shows a marked change in its air equivalent for even the high ranges. The statement of McClung, Levin and Rutherford that equal successive layers of aluminium foil diminish the range by equal amounts seems to hold true for thin sheets of foil when the range is high; but when the metal sheet is thicker, or for thin sheets when the range is low, it does not hold. The slight difference however in the air equivalent of the thin foil when near the polonium and when farther away from it would scarcely be detected by measuring directly the air equivalents in the two positions. This is probably the explanation of the above statement by McClung, Levin and Rutherford, since their determinations were made in this direct way.

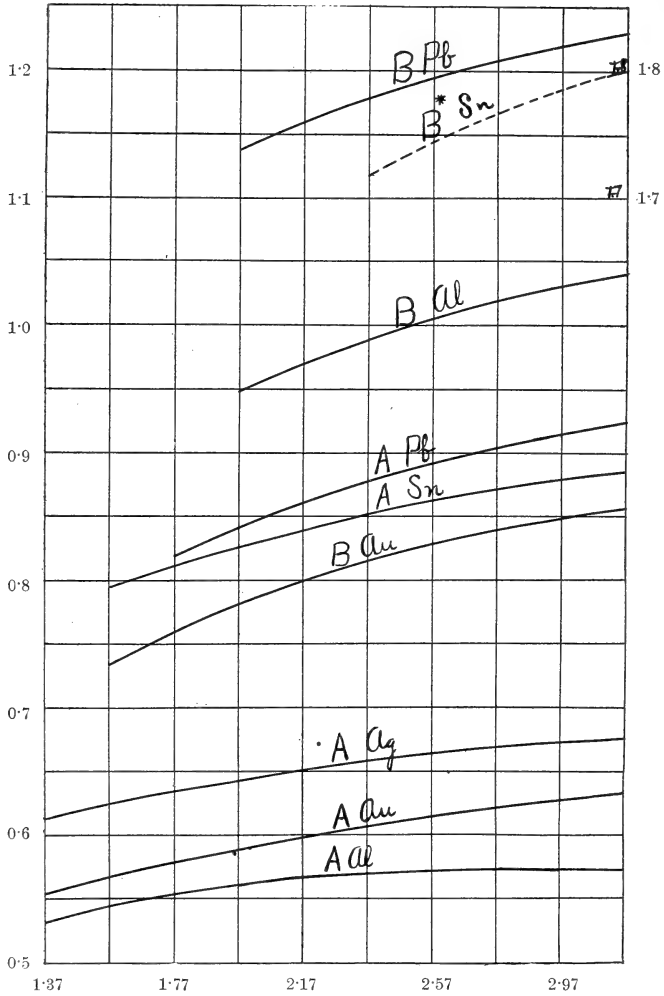

FIG. 4. The abscissas are the ranges in air of the *a* particles when they enter the metal sheets; the ordinates the air-equivalents of the metal sheets. The curve for B Sn has the ordinates from 1·718 to 1·80 as indicated on right-hand side of the figure instead of 1·118 to 1·20 as shown on left-hand side.

Since the air equivalent does decrease with the range of the *a* particle entering it, the ratio of the air equivalent to the thickness of a given sheet of metal should be less than the same ratio for a thinner sheet of the same metal. This is shown to be true by the last column of Table II. From the curves in figure 4, we see that the change is more pronounced the thicker the metal foil and the heavier the metal.

The possibility that the observed variations in the ionization may be due to secondary rays is precluded by the fact that numerous direct determinations of the Bragg ionization curves with the metal sheets near the polonium and again near the ionization chamber showed no irregularities in the curves, as would be expected were secondary rays present in any appreciable amount.

Thus far, from a comparison of the data given in Table III and represented graphically in figure 4, I have been unable to deduce any definite statement relative to the rate of change in the air equivalents, except that, for the same metal, the thicker the foil the more marked is the change and that, for sheets of different metals of about the same air equivalents, the rate of change is in the order of their atomic weights; (i. e., Al, Ag, Sn, Au, Pb). Further experiments are in progress and it is hoped that they will furnish the desired information, when completed.

In conclusion, I wish to express my gratitude to Prof. Bumstead, at whose suggestion these experiments were undertaken, for his valuable suggestions, and interest in the work; also to Prof. Boltwood, who kindly prepared the polonium for me and gave me many helpful suggestions.

Results.

The air equivalents of metal foils decrease with the range (i. e., with the speed) of the *a* particles entering them. The change is very small for thin foils of the lighter metals when the range of the *a* particles is high; but, when the range is low for thin sheets, or when the sheets are thicker, the change becomes quite marked. In comparing the change for sheets of different metals of nearly equal air equivalents, the rate of change is seen to be in the order of the atomic weights of the metals.

New Haven, Conn., June 15, 1908.

ART. XXII.—*Notes on the Lower Paleozoic Rocks of Central New Mexico*;[*] by WILLIS T. LEE.

THE lower Paleozoic rocks are exceptionally well exposed in the Caballos Mountains of central New Mexico. Gordon and Graton[†] refer to them in a description of the lower Paleozoic formations in New Mexico, but attention is confined by these writers principally to other parts of the territory, and the occurrence, especially of the Cambrian and the Ordovician formations, in the Caballos Mountains, as well as their relations to each other and to the overlying rocks, are of sufficient interest to warrant the more definite statements contained in this paper.

The Caballos Mountains form one of the small mountain groups of central New Mexico and occur west of the town of Engle between the Rio Grande and the Jornado del Muerto. The northern part of the mountains consists of a faulted block tilted to the east and the sedimentary formations outcrop in the precipitous western face. The lower part of the slope consists of granite, above which occur the Cambrian, Ordovician and Carboniferous rocks as shown in the following section measured about three miles north of Shandon, a mining camp on the Rio Grande. With the Cambrian and Ordovician of this section are correlated similar rocks observed in other parts of the Rio Grande Valley.

A few species of fossils were found in the Cambrian sediments, and these have been identified by Dr. C. D. Walcott of the Smithsonian Institution. Fossils collected from the Ordovician rocks have been examined by E. O. Ulrich of the United States Geological Survey, and the quotations given in the paper are from his written report. The Ordovician fossils are not well preserved and specific identification is difficult.

A thickness of 1000 feet or more of the granite is exposed in the cliffs. The rock is massive and coarsely crystalline, although schist and gneiss occur in some places. Its surface was apparently eroded in early Cambrian time to a nearly level plain upon which the sedimentary rocks were deposited. The coarse-grained and, in some places, conglomeratic quartzite at the base of the Cambrian grades upward into the green shale, in which the Cambrian fossils occur in great abundance at several horizons, some close to the basal quartzite, others near the top.

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[*] Published by permission of the Director of the U. S. Geological Survey.

[†] Gordon, C. H. and Graton, L. C., Lower Paleozoic Formations in New Mexico, this Journal, xxi, pp. 390–395, 1906.

Section of Rocks exposed in the Caballos Mountain three miles north of Shandon, New Mexico.

No.		Ft.
(1)	Limestone, blue, massive, fossiliferous, in thick plates separated by dark colored shales (age, lower Pennsylvanian)	600
(2)	Limestone, cherty in places, white to brown (age not determined)	500
(3)	Limestone, cherty, massive, cliff-making. The following fossils occur near the top: *Rafinesquina* cf. *kingi*, *Plectambonites saxea*, *Plectambonites* n. sp., *Favosites asper*, *Zygospira recurvirostris* (Richmond mutation), *Rhynchotrema capax* (age, late Ordovician)	600
(4)	Shale, dark green, containing *Obolus* (*Westonia*) *Stoneanus* Whitfield, *Obolus sinoe* Walcott? (The following fossils were found in talus derived apparently from this horizon: *Plectorthis desmopleura* Meek, *Obolus sinoe* Walcott, *Lingulella acutangula Roemer?* (age, upper Cambrian)	90
(5)	Quartzite	10
(6)	Granite	?

Cambrian sediments occur also in Cerro Cuchillo, a hill consisting of rocks faulted and tilted steeply to the east, that stands a few miles west of the Rio Grande near the northern end of the Caballos Mountains. The rocks were probably originally continuous with those of the Shandon region, but the two exposures are 20 miles apart and are separated by a zone of profound faults. Here, as in the Caballos Mountains, the Cambrian sediments are about 100 feet thick and consist of a basal quartzite resting on granite and overlain by greenish shale in which were found fragments of trilobites and the same species of brachiopods found near Shandon. The shale is overlain by cherty limestone similar to the Ordovician of the Caballos Mountains but no fossils were collected from it.

The Ordovician rocks of the Caballos Mountains are apparently conformable with the Cambrian, but as shown below, there is probably a considerable time-break between them. They consist of massive cherty limestone and form a conspicuous cliff 600 feet high. The rocks of undetermined age above are less cherty and not so massive, but in some places can be distinguished from the lower chert only by careful examination, the two forming a single cliff 1100 feet high. The fossils from the lower chert indicate Richmond or late Ordovician age, and in the absence of evidence, the upper chert also may be late Ordovician or it may be Silurian.

The chert is overlain in the Caballos Mountains by 600 feet of limestone of Pennsylvanian age. No fossils of intervening age were obtained and it is possible that both Mississippian and Devonian rocks may be found here, for they are known to occur at Lake Valley and at Hillsboro, a few miles to the west.*

About eight miles south of Shandon near the south end of the Caballos Mountains, the older Paleozoic rocks are again exposed, although considerably folded and faulted. No detailed section of them was made owing to their disturbed condition, but the following generalized section with estimated thicknesses indicates their order of succession:

Section of Rocks exposed near Red Cabin, eight miles south of Shandon, New Mexico.

No.		Thickness estimated. Ft.
(1)	Limestone, blue (age, lower Pennsylvanian)	500
	Unconformity of erosion.	
(2)	Shale, black (age, Devonian (?))	1–300
(3)	Limestone, cherty (age, late Ordovician)	500
	Angular unconformity.	
(4)	Limestone, cherty (age, early Ordovician)	200
(5)	Quartzite (age, not determined)	300
	(Base not exposed.)	

A few fragmentary fossils were found in the cherty limestone (No. 4) of the Red Cabin section. Although they are very poorly preserved, Ulrich recognizes them as *Ophileta* cf. *complanata* and *Hormotoma* cf. *artemisia* (Billings species) and refers them with some confidence to the lower Ordovician (Beekmantown).

Cherty limestone about 500 feet thick, that is probably equivalent to the lower chert (No. 3) of the Shandon section, lies unconformably upon the early Ordovician chert in some places and upon the massive quartzite (No. 5) of the Red Cabin section in other places. Fossils were collected from it at the base, near the middle, and at the top, but as Ulrich includes the three lots in one general fauna, they may be combined as follows, together with his notes concerning them:

Rafinesquina, n. sp. (characteristic of Western Richmond).
Rhynchotrema capax (most characteristic Richmond fossils).
Favosites asper (late Ordovician and Clinton).
Petraia, sp. undet.
Lindstromia, sp. undet.
Dalmanella (*?Schizophoria*), sp. undet.

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* Gordon, C. H. and Graton, L. C., Lower Paleozoic Formations in New Mexico, this Journal, xxi, pp. 394–395, 1906.

Streptelasma or *Petraia,* sp. undet. Specimen shows only the exterior. So far as can be seen it recalls Silurian species rather than Ordovician.

Nematopora, cf. *granosa* Ulrich, a Trenton species of Minnesota.

Schuchertella sp., closely allied and possibly the same as the Silurian *S. subplana* (Conrad).

Fragments of a brachiopod recalling Silurian species of *Strophonella.*

Small subcircular orthoid, suggesting relations to *O.* (*Rhipidomella*) *hybrida.*

Atrypoid brachiopod, possibly *Zygospira* but distinct from all American species of that genus known.

Brachiopod of undetermined affinities. In its general aspect it recalls Russian species of *Porambonites*, but the surface of the shell is not porous.

Ctenodonata, sp. undet.

Lophospira, cf. *gyrongonia* McCoy and *medialis* Ulrich.

Lophospira, sp. allied to *gyrongonia* McCoy.

Fragment of a gastropod, apparently of the same species as the Clinton form doubtfully referred by Foerste to *Euomphalus sinuatus* Hall.

Trochonema, n. sp.

Eunema sp. near *E. robbinsi* Ulrich.

Eccyliomphalus, sp. undet. A small, incomplete example of a closely coiled species reminding of *E. gotlandicus* Lindstrom and *E. contiguus* Ulrich, the former Silurian, the latter middle Ordovician.

Loxonema? The specimen is a fragment (consisting of the greater part of two whorls) reminding rather strongly of the *L. murrayanum* described by Salter from Black River limestone in Canada.

In a local uplift about one mile west of Red Cabin, I found the following fossils in chert that is presumably the same as that of No. 3 of the Red Cabin section:

Calopoecia canadensis
Favosites asper
? Columnaria alveolata
Platystrophia dentata var.
Petraia
Lindstromia
Dalmanella (*? Schizophoria*)
Lophospira
Loxonema.

South of Red Cabin, about two miles and five miles respectively, the latter locality about six miles northwest of Rincon, 300 feet of cherty limestone is exposed at the foot of the cliffs. The rocks are continuous with the upper chert (No. 3) of the Red Cabin section and yielded the following fossils:

Petraia, sp. undet. (near *Streptelasma profundum* (Black River) and *S. caliculuris* (Silurian)).
Lindstromia, sp. nov.
Orthis, near *davidsoni* and *flabellum.*
Dalmanella (*? Schizophoria*), sp. undet.
Clorinda? sp. undet.
Atrypa sp. nov. (near *Zygospira putilla* and *Atrypa marginalis*).
? Euomphalus sinuatus (Hall) Foerste (Clinton species).
Lophospira, sp. undet.
Trochonema " "
Eunema, near *robbinsi*, a Trenton form.
Loxonema
Nucleospira?

Ulrich states that all of the fossils from near Red Cabin, with the exception of the two lower Ordovician forms, belong at the same general horizon and are of Richmond or late Ordovician age, and suggests that the absence of fossils indicating Ordovician horizons intervening between this and the early Ordovician rocks below the uncomformity "probably points to conditions similar to those prevailing in the vicinity of El Paso 75 miles to the south, where the Richmond commonly rests directly on Beekmantown." Since a lower Ordovician chert occurs unconformably below the Richmond in the Red Cabin section, and this in turn rests upon a massive quartzite that is not represented in the Shandon section, it is probable that the apparent conformity of the Cambrian and Ordovician in that section is deceptive and that a time interval of considerable duration is represented between the two formations.

According to Ulrich, there are certain elements in the faunas that suggest Silurian rather than Ordovician age, but, excepting the two early Ordovician species, he is inclined to regard the fauna as representing one of the phases of the Western Richmond. He states that "very few of the species are closely related to ordinary described American forms, but they are very similar and perhaps identical with species occurring in the Borkholm limestone of the Russian Baltic Provinces. In the absence of authentic examples of the Russian species, I hesitate as yet to identify these New Mexican fossils with them. The associated coral bed represented west of Red Cabin, however, is widely distributed in America west of the Mississippi and occurs also in the Island of Anticosti. Its position is within the upper part of, or just above, the Maquoketa shale of the Mississippi Valley. The highest horizon represented east of Red Cabin and also north of Rincon, may be correlated more or less definitely with the Maquoketa shale and this with the upper Richmond of Ohio and Indiana."

No fossils were found in the black shale (No. 2) of the Red Cabin section, and it may be Devonian as stated by Gordon and Graton.* It is apparently this shale that these writers have in mind when they state that the Devonian is represented in the Caballos Mountains, although it does not appear from their descriptions that fossils were found or other evidence of age except stratigraphic position obtained. The overlying Pennsylvanian limestone rests in some places upon this shale, in other places upon the Richmond chert, as shown in the Red Cabin section, and in still other places upon the chert overlying the Richmond, as in the Shandon section. No rocks of Mississippian age were found, but their occurrence a few miles to the west suggests that the Mississippian limestones once extended over this region and that they, together with the greater part of the Devonian, were removed by erosion previous to the deposition of the Pennsylvanian sediments.

A small exposure of cherty limestone was found beneath the Pennsylvanian limestone in the northern slope of the Robledo Hills about 15 miles south of Rincon. In this chert I found the following fossils:

Lophospira, two small undet. species.
Lophospira, ? larger species.
Trochus ? sp. undet.
Bucania ? sp. undet.
Trochonema, sp. undet.
Eotomaria, sp. undet.
Pentameroid shell agreeing with *Sieberella*, except that it has no fold nor sinus.

Ulrich regards these as constituting a part of the Richmond fauna just described, but states that they are clearly distinct from other Richmond faunas so far as known from the west and southwest. His statement that more perfect fossils may prove that the fauna is Silurian finds support in the occurrence of Silurian rocks in the Franklin Mountains 35 miles to the south.† A thickness of only a few feet of the rocks is exposed in the Robledo Hills and their relations to other formations could not be determined.

A summary of the foregoing statements regarding the lower Paleozoic rocks of central New Mexico may be given as follows: (1) Rocks of upper Cambrian age about 100 feet thick rest upon an eroded plane of granite. (2) Rocks of early

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* Ibid., p. 391.

† Richardson, G. B., U. S. Geol. Survey, El Paso Folio.

Ordovician (Beekmantown) age occur in some places, but are apparently absent in other places. (3) Rocks of Richmond age are well developed and rest in some places upon Beekmantown and in other places apparently upon Cambrian. (4) The Richmond is separated from the Beekmantown by an unconformity that apparently represents a long time interval. (5) Certain elements in the fauna which is here described as Richmond are suggestive of Silurian rather than Ordovician age, and some of the cherty limestone may belong in the Silurian system. (6) Rocks of possible Devonian age occur in the Caballos Mountains, but no fossils were found in them. (7) No Mississippian rocks were found and Pennsylvanian limestones rest in some places upon the Devonian (?) shale and in other places upon the Ordovician chert.

ART. XXIII.—*On Kaersutite from Linosa and Greenland*; by HENRY S. WASHINGTON; *with Optical Studies by* FRED. EUGENE WRIGHT.

Introductory Note.—While visiting the small island of Linosa, off the coast of Tunis, for the Carnegie Institution in the summer of 1905, I found small crystals of a black amphibole, accompanied by others of a glassy white, cleavable mineral, apparently a feldspar,* among the lapilli of a small, parasitic cone of Monte Rosso.† The presence of amphibole crystals here had previously been noted by Speciale.‡ Similar crystals were also said to be found near I Faraglioni, but this locality was not visited. Apart from these occurrences, amphibole is quite unknown in the lavas of Linosa, but the peculiar, triclinic aenigmatite (cossyrite) is met with, though not abundantly, and a kaersutite-like hornblende as well, in the lavas of the near-by island of Pantelleria.

Chemical analysis showed that the Linosa hornblende is very high in titanium, and that in this, as well as in other respects, it closely resembles the kaersutite of Greenland, which was partially described in 1884 by Lorenzen.§ A comparative investigation of the two minerals was therefore determined on, the chemical work being done by me and the optical determinations being very kindly undertaken by Dr. Wright, to whom I am deeply indebted for his valuable and hearty collaboration. Through the kindness of Professor N. V. Ussing, of Copenhagen, we obtained a piece of one of the best of Lorenzen's original specimens of kaersutite, and we take this opportunity to express our sincere thanks to him for his courtesy and great liberality, without the aid of which the comparison would have been sadly incomplete.

The Linosa Amphibole.

Physical Characters.—The Linosa amphibole is monoclinic in crystal system and prismatic in habit. It occurs in roughly developed crystals and fragments from 5 to 20^{mm} long by 3 to 8^{mm} thick, and bounded by the faces of the unit prism *m* (110) and the clinopinacoid *b* (010). Terminal endings are usually absent, but a few of the crystals show the common forms *p* ($\bar{1}01$) and *r* (011), which, however, were too imperfect to admit of accurate measurement with the goniometer. Cleavage parallel to *m* (110) is highly perfect, giving an angle of 55° 22′

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* A description of this mineral will be given in a separate paper.

† H. S. Washington, Jour. Geol., vol. xvi, p. 10, 1908.

‡ S. Speciale, Boll. Com. Geol. Ital., vol. xv, p. 2, 1884.

§ J. Lorenzen, Medd. Grönl., vii, p. 27, 1884.

(Wright) with observed limits of ± 2′, measured on cleavage fragments with a two-circle goniometer with reducing attachment. The reflection signals were fairly sharp and satisfactory. No cleavage or parting after 100 or 001 was noted with certainty, and whenever cleavage is not developed the fracture is conchoidal. The hardness is 6 and the mineral is very brittle. Before the blowpipe it fuses readily to a black, slightly magnetic bead.

1

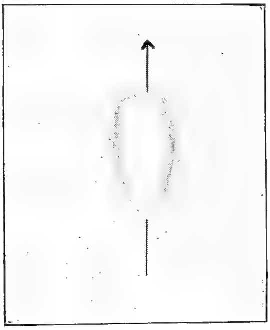

Fig. 1. Kaersutite from Linosa. Etch pit on 110, HF. × 480.

The specific gravity was carefully determined with the pycnometer on about 2 grams of selected fragments, entirely free from adhering bits of scoria or feldspar and quite free from inclusions so far as could be seen with a lens. With this material the density at 13° was found to be 3·336 (Washington), a figure which may be accepted as representing the true value.

Etch figures on *m* (110) were produced by immersing cleavage fragments in hot commercial hydrofluoric acid (on a steam bath at 100°) for a period of 30 seconds. Further action was stopped by plunging the platinum basket containing the fragments into cold water. Under these conditions of experiment well-formed etch pits resulted, from 0·01 to $0·04^{mm}$ long and about half as wide. Different stages of development are illustrated in figures 1–3, which are reproductions of photomicrographs of the figures in reflected light. In each case the vertical edge of the photograph is parallel to the prism-axis. A comparison of these figures with those obtained by Daly,* and later by Wright,† shows that they resemble in certain features the

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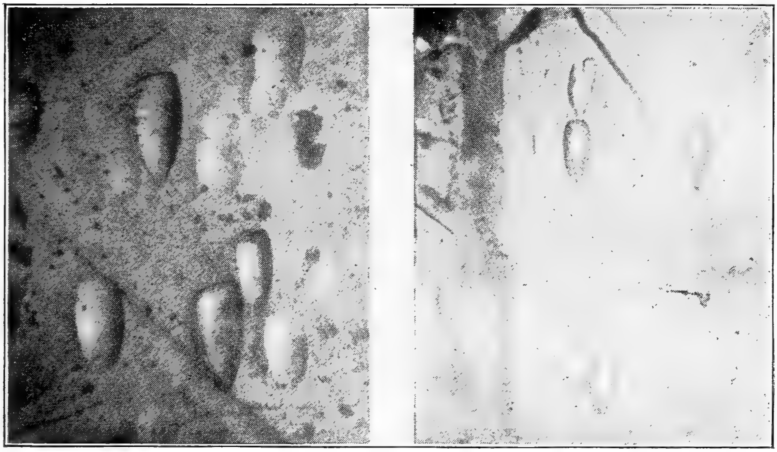
* R. A. Daly, Proc. Amer. Acad. Arts and Sci., vol. xxxiv, pp. 333–429, 1899.

† F. E. Wright, Tschermak's Min. Petr. Mitth. vol. xix, pp. 308–320, 1899.

pits formed on lustrous basaltic hornblende and in other particulars the etch figures on barkevikitic hornblende. The etch figures on the faces of the prism zone prove with certainty that the mineral is monoclinic, and that it belongs in the general group of the dark, highly ferruginous, aluminous amphiboles, which are commonly referred to the hornblendes.

Optically, this amphibole is remarkable in several of its properties. The color is an intense jet black, with highly vitreous, splendent luster. The streak is light brown. In common with amphiboles of this group, it is brown to pale brown in transmitted light, and is strongly pleochroic: $\mathfrak{c}$ = dark brown, almost opaque, $\mathfrak{b}$ = brown, $\mathfrak{a}$ = pale olive brown or olive green; absorption, $\mathfrak{c} > \mathfrak{b} > \mathfrak{a}$. The natural color of the mineral is so deep and the pleochroism so strong that the normal interference colors are greatly modified, and the observation of the optic axes and similar optical phenomena is considerably hindered.

2 3



Figs. 2, 3. Kaersutite from Linosa. Etch pits on 110, HF. Fig. 2, × 360; fig. 3, × 240.

Owing to the extreme brittleness of the cleavage fragments, it was found difficult to prepare sections parallel to the clinopinacoid, and the extinction angle was measured only on the cleavage face *m* (110). By using the etch figures as a basis for orientation, the extinction angle $c \wedge \mathfrak{c}$ was found to be +1·4° (in the acute angle β) in white light,* as indicated by the arrow in figure 1. This direction presupposes the standard crystallographic orientation of the amphiboles by Tschermak. This extinction angle is noteworthy because of its positive character, and it is readily discernible, although so small that (in the absence of corroborative data) it might be considered to be due to observational error alone in the deep-colored flakes. The dispersion of the bisectrices is very slight, and practically the same value was obtained by using sodium light as that for white light. In convergent polarized light the interference phenomena are only moderately clear and distinct. The optic axes lie in the plane of symmetry (010), and the optical character is negative.

The refractive indices were determined on a very perfect cleavage flake with an Abbé total refractometer, a solution of sulphur in methylene iodide, with refractive index 1·7882, being used. The observations were made in sodium light, and the following values obtained:

	Average angle observed.	Equivalent refractive index.
$\gamma =$	67° 18′	1·760
$\beta =$	65° 8′	1·730
$\alpha =$	62° 33′	1·692

$\gamma - \alpha = 0·068$, $\gamma - \beta = 0·029$ $\beta - \alpha = 0·039$

The optic axial angle calculated directly from these refractive indices is 2V = 79° 54′.

The boundary shadow for α was much more distinct than those for β or γ, and could be determined with greater accuracy. In the values given for β and γ an error of ± 0·002 is easily possible. The fact that light waves vibrating along $\mathfrak{c}$ and $\mathfrak{b}$ were strongly absorbed undoubtedly exerted an influence on the relative intensity of the phenomena observed, and caused the faintness of the β and γ curves of total reflection.

A somewhat smaller value for 2V was obtained by measuring the angle of the optic axes directly in another section cut approximately normal to the acute bisectrix, by the method described by Wright.† The deep color of the mineral impaired the accuracy with which the determinations of the positions of the optic axes could be made, so that the results are but approximate at best. In two different portions of the same section thus measured the values 2V = 71° and 72° were obtained.

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* Average of 10 measurements, with observed limits ±0·6°.

† F. E. Wright, this Journal, vol. xxiv, p. 317, 1907.

While in general the probable error for this method should not exceed 2°, the intense color of the amphibole has evidently affected this limit appreciably, as it is not probable that differences exist in the chemical composition of the material sufficiently great to cause the optic axial angle to vary 9°. The optic axial angle apparently lies between the two extremes, 71° and 79° 54′, but it is thought that the latter more closely approaches the true value.

Chemical Composition.—For the chemical analysis several grams of selected crystal fragments were coarsely crushed, washed free from dust, and the material (dried at 110°) carefully picked out under a lens. The only adherent impurities were feldspar, limonite, and particles of the scoria, and all fragments showing traces of these were excluded. Thin sections of fragments showed but very few small inclusions of magnetite, but these were separated by treatment with an electromagnet, only a very small amount being thus extracted. It is believed that the material as finally pulverized for analysis was practically free from extraneous matter. Treatment with acid for purification was not resorted to, as the mineral is partially decomposed by acids.*

The methods of analysis employed were those advocated by Hillebrand† and the writer,‡ about one gram being taken in each case for silica, alumina, etc., and for the alkalies; about one-half a gram for ferrous iron; and 0·8 gram for fluorine. The alkalies were determined by Lawrence Smith's method, titanium colorimetrically (a mean of three closely agreeing determinations), and manganese by precipitation with bromine. Ferrous iron was determined twice by the simple Pratt method, freshly standardized permanganate solution being used. The figure given (3·96) is the mean of 3·99 and 3·94. These results indicate that there was no appreciable oxidation of the FeO in the finely ground powder during the interval of a year which elapsed between the two determinations.

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* In a recent criticism (Geol. Mag., dec. v, vol. iv, p. 161, 1907) of a previous paper of mine, Mr. T. Crook says that evidence is needed of the absence of inclusions of ilmenite, etc., in this hornblende, and he expresses doubts as to "the view that titanium enters vitally and in any serious quantity into the composition of ordinary ferromagnesian minerals." The amount of TiO_2 found would imply, if existent only as ilmenite, the presence of 17 or more per cent of this, and it is hoped that the details given here will suffice to show that but minimal amounts, if any, of ilmenite or titaniferous magnetite were present. As regards his latter doubt, Mr. Crook seems to be unaware of much recent and highly trustworthy work which has been done in chemical mineralogy, and which proves conclusively that titanium does enter vitally and often in considerable amount into the composition of the ferromagnesian minerals.

† W. F. Hillebrand, Bull. No. 305, U. S. Geol. Surv., 1907.

‡ H. S. Washington, Manual of the Chemical Analysis of Rocks, New York, 1904.

SiO_2	40·85	·681
TiO_2	8·47	·106
ZrO_2	none	
Al_2O_3	9·89	·097
Fe_2O_3	8·85	·056
FeO	3·96	·055
MnO	0·12	·002
NiO	0·10	·001
MgO	12·47	·312
CaO	12·16	·217
BaO	none	
Na_2O	2·01	·032
K_2O	0·63	·007
H_2O	0·19	·010
F	0·28	·007
	99·98	

Hornblende from Linosa.* Washington, analyst.

In its general features, this analysis closely resembles many analyses of basaltic hornblendes, such as those made by Schneider.† Alumina is, however, decidedly lower, and a most striking character is the very high percentage of TiO_2, the amount of which is nearly twice that reported for most basaltic hornblendes. The character of the material used for the analysis precludes the possibility that this high figure is due to admixture of titaniferous magnetite or ilmenite, as no appreciable amount of such inclusions could have been present, so that the titanium must be regarded as belonging to the hornblende molecule. The analysis will be discussed later, in connection with others, and attention need be called here only to the figures for the iron oxides and the percentage preponderance of ferric over ferrous oxide.

The Kaersut Amphibole.

Occurrence.—A peculiar, highly titaniferous amphibole from Kaersut, Nugsuaks Peninsula, on the shore of Umanak Fjord, Greenland, was described by J. Lorenzen,‡ who called it kaersutite. According to Steenstrup (as quoted by Lorenzen), the kaersutite occurs in a vein or dike, 2 to 6 inches wide, which cuts a horizontal sheet of peridotite 120 feet thick. It is accompanied by plagioclase, titaniferous ore, an astrophyllite-like mica, and some pyrite, with zeolites, calcite, and quartz as secondary minerals. This sheet of peridotite is

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* This analysis has been published in Rock Minerals, by J. P. Iddings, New York, 1906, p. 330.

† C. Schneider, Zeitschr. Kryst., vol. xviii, p. 580, 1890.

‡ J. Lorenzen, Medd. Groenland, vol. vii, p. 27, 1884.

undoubtedly the same as that mentioned by Phalen* in his description of the rocks of the Nugsuaks Peninsula, who speaks of it as forming a cliff 200 feet high, calls it picrite, and gives a petrographic description. The kaersutite-bearing vein is not mentioned by him.

The specimens sent us by Professor Ussing show a rather coarsely granular mass of feldspars pierced in all directions by prisms of the black hornblende, which run up to 3^{cm} in length by 5^{mm} in thickness. The rock is far from fresh, and is stained brown and yellow with iron, and here and there a pale green. Small grains of magnetite or ilmenite and many apatite crystals in water-clear prisms 5^{mm} in length are present, and a few small specks of pyrite were seen, but we could not detect with certainty any of the mica megascopically.

In thin section the texture is distinctly that of a granitoid rock rather than that of vein material. The structure is decidedly miarolitic. The most abundant mineral is a plagioclase, in anhedral development, whose extinction angles indicate the average composition Ab_1An_2. (Extinction angle on 001 = 13°; γ about 1·570 and α slightly $>$ 1·56.) With this is some alkali-feldspar, which shows some microperthitic features and is apparently highly sodic, though it is mostly cloudy and considerably decomposed. The brown kaersutite prisms are prominent, and show the optical properties to be described later. Small stout prisms of fresh augite are not uncommon. For the most part they are colorless in the interior and slightly greenish toward the border, but there are also some small anhedra of a highly pleochroic, brilliant grass-green augite which occasionally forms a border about the less colored variety, and is apparently the chromiferous augite mentioned by Ussing.† Indications only of the violet augite described by Ussing were observed by us.

Small thin plates of light brown biotite occur. These are intensely pleochroic, the color for rays vibrating parallel to the cleavage cracks being a very deep purplish red, while perpendicular to this they are pale yellowish brown. They show no analogy with astrophyllite. Some small grains of opaque ore are present, but these only rarely occur as inclusions in the hornblende and no pyrite was visible in our sections. Deep red goethite was observed as an alteration product of the magnetite or pyrite. Apatite is very abundant, in long, clear prisms, and is a frequent inclusion in the hornblende. It was also noted by Ussing as an abundant constituent. Patches of greenish chlorite minerals occur and are the cause of the occasional green color of the rock.

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* W. C. Phalen, Smithson. Misc. Coll., vol. xlv, p. 194, 1904.

† In Rosenbusch, Mikr. Phys., vol. i, pt. 2, p. 237, 1905.

A hornblende which apparently resembles that of Kaersut is described by Phalen* as occurring in a fine-grained quartz-monzonite at Alanekerdlak on the Nugsuaks Peninsula. From our examination of the original specimen, kindly loaned by Dr. G. P. Merrill of the Smithsonian Institution, it appears that, while the rock resembles that of Kaersut, except in its finer grain, this hornblende differs from ours, being of a yellow-brown rather than a red-brown color, and with somewhat different pleochroism. The optical characters were not determined, but it would appear to be titaniferous and related to that which we are describing.

Physical Properties.—The Kaersut amphibole is monoclinic and forms prisms which reach a length of 3^{cm} and thickness of 5^{mm} in our specimens. They are bounded by the prism *m* (110) and the pinacoid *b* (010). The terminations are usually poor, but some crystals show the presence of steep domes or pyramids, whose symbols could not be determined. These are also to be seen in the thin sections. Ussing† gives (110), (011), ($\bar{1}01$), and more rarely ($\bar{1}21$) and (010), as the forms observed by him. Twinning was observed in several of the sections. In one case the twinning plane was probably a steep dome, making an angle of 13° with the cleavage lines, and showing in several places several narrow lamellae due to repeated twinning. The cleavage lines cut this twinning trace uninterruptedly. This crystal is shown in fig. 4, from a photograph kindly made for us by Prof. J. Volney Lewis. The extinction is parallel to the right of the twinning line and 17° to the left. The crystals are seen in thin section to be frequently crossed by narrow cracks (seen as dark lines in the figure). Some of these are irregular, but many are straight and parallel, crossing the cleavage lines of 110 at about 32°. For the angle $110 \wedge 1\bar{1}0$ measured on the cleavage surfaces, Lorenzen (p. 29) gives 55° 29′ (the mean of 55° 25′ and 55° 33′), while Ussing obtained 55° 35′. On an excellent cleavage piece, giving sharp reflexion signals, Wright obtained 55° 35′, while on less satisfactory fragments the values were 55° 34′ and 55° 23′. We therefore consider that 55° 35′ best represents the value. For other angles Ussing gives the following: $\bar{1}01 \wedge 011 = 34° 16'$, $\bar{1}01 \wedge \bar{1}10 = 76° 51'$ $110 \wedge 011 = 68° 44'$. The cleavage is highly perfect, and where it is not developed the fracture is conchoidal. We found the hardness to be about 6; Lorenzen gives it as 5·5. The mineral is very brittle, and fuses readily before the blowpipe to a dark, magnetic bead.

The specific gravity as determined by Washington with the pycnometer on about one gram of very carefully selected frag-

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[*] W. C. Phalen, loc. cit., p. 207.

[†] N. V. Ussing, in Rosenbusch, Mikr. Phys., vol. i, pt. 2, p. 236, 1905.

ments was 3·137 at 25° C., while Ussing obtained 3·237 (temperature not stated) and Lorenzen 3·04 at 18°.

The extinction angle on *m* 110 was found to be $c : \mathfrak{c} = -7{\cdot}8°$ in the obtuse angle β, measured in sodium light (an average of 14 readings on different sections). In Li light the extinction was $c \wedge \mathfrak{c} = -9{\cdot}3°$, which would indicate that there is some slight dispersion of the bisectrices with $c \wedge \mathfrak{c}_{Na} < c \wedge \mathfrak{c}_{Li}$. That it is slight, however, is evident from the comparatively sharp position of extinction in ordinary light. Ussing gives the extinction angle as $c : \mathfrak{c} =$ about 10° in the obtuse angle β, but does not state whether this was measured on 010 or 110. He remarks that it is somewhat greater for red than for green, which is in accord with the observations of Wright. The plane of the optic axes is the clinopinacoid.

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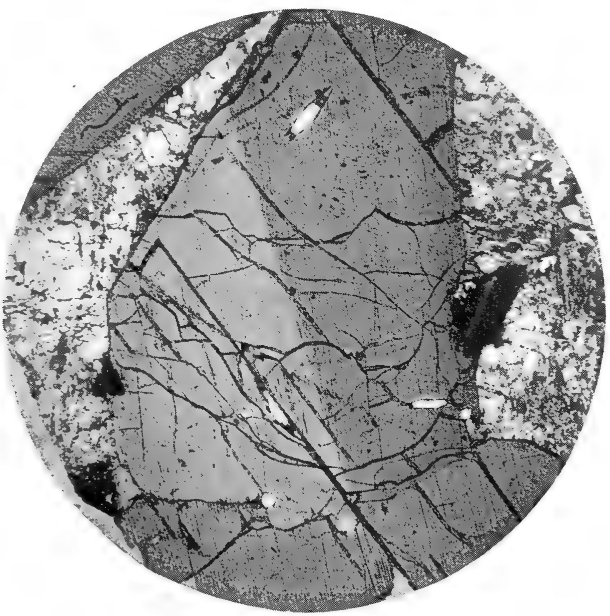

The refractive indices were determined directly by the method employed in the preceding case, and were found to be as follows: $\alpha = 1{\cdot}676$, $\beta = 1{\cdot}694$, $\gamma = 1{\cdot}708$, the probable error being less than $\pm\, 0{\cdot}02$. This gives for the birefringences: $\gamma - \alpha = 0{\cdot}032$, $\gamma - \beta = 0{\cdot}014$, $\beta - \alpha = 0{\cdot}018$. The optic axial angle calculated from these indices is $2V = 82°\ 6'$, while measurement of a section nearly perpendicular to the

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FIGS. 5, 6, Kaersutite from Kaersut, Greenland. Etch pits on 110, HF; × 120.

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FIG. 7, Kaersutite, Kaersut, Greenland. Etch pits on 110, HF ; × 480 acute bisectrix on the universal stage gave 2V= 81°. This value can be considered only fairly accurate because of the deep color of the mineral which tends strongly to veil the optical phenomena, but it agrees satisfactorily with the calculated value, much better, indeed, than in the case of the Linosa hornblende.

Chemical Composition.—The chemical analysis was carried out on about 2 grams of carefully selected fragments, which, after crushing and washing free from dust, were treated with an electro-magnet to remove the few particles which contained ore grains. The microscope indicated that but few of these were present as inclusions, and the very small amount thus removed is in harmony with the observations. The only inclusions of note are of apatite, the needles of which penetrate the hornblende to a very considerable extent. As the mineral power was somewhat acted on by acid it was thought best not to remove these inclusions by its use, but to correct the analysis for their presence by determining P_2O_5. Apart from these apatite inclusions the material analyzed was extremely pure, as is shown in fig. 4, in which the enhedral apatites are well seen. It was dried at 110° prior to the analysis, which was carried out by the methods adopted in the previous one.

Lorenzen (p. 30) seems to have had great difficulty, using Doelter's method, in decomposing the mineral with sulphuric and hydrofluoric acids to determine FeO and Fe_2O_3. He reports the value FeO = 6·61 per cent in one case, but prefers to consider all the iron as ferrous in the statement of his analysis. Using the simple Pratt method, I had no difficulty in the solution of the finely powdered mineral in six minutes, and the result given here may be accepted as fully as correct as in the case of the Linosa hornblende, though the amount on hand did not permit of a duplicate determination.

Special search was made for tin, as 0·26 per cent SnO_2 was reported by Lorenzen, but with absolutely negative results. The method adopted was essentially that of Baley as outlined by Classen.* The mineral powder was decomposed by evaporation to dryness with nitric and hydrofluoric acids, which would not lead to loss of tin by volatilization as tin fluoride is decomposed by heating. The residue was dissolved in hot dilute hydrochloric acid, filtered, and the filtrate treated with pure zinc, which would precipitate any tin. Only a very slight residue remained, which was wholly soluble in nitric acid. Neither this solution nor the previous filtrate gave any precipitate with H_2S or other reaction for tin. We therefore consider that our hornblende contains no tin, and that the

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* A. Classen, Ausgew. Method. Anal. Chem., i, 1901, p. 184.

presence of tin, as reported by Lorenzen, is very doubtful and certainly cannot be considered as characteristic of the mineral, as suggested by him.

Lorenzen's original analysis and the new one are given below, the last two columns showing the figures of the latter as corrected for the 0·77 per cent of apatite present and recalculated to 100 per cent, and the molecular ratios.

	I	II	III	IV
SiO_2	41·38	39·30	39·52	·659
TiO_2	6·75	10·25	10·31	·129
SnO_2	0·26	none	none	
Al_2O_3	14·41	11·16	11·22	·110
Fe_2O_3	none	1·21	1·22	·008
FeO	11·28	8·76	8·81	·122
MnO	n. d.	0·06	0·06	·001
NiO	n. d.	none	none	
MgO	13·51	13·24	13·31	·333
CaO	12·97	11·29	10·93	·195
Na_2O	n. d.	2·93	2·95	·048
K_2O	n. d.	1·06	1·07	·011
H_2O	n. d.	0·59	0·59	·033
P_2O_5	n. d.	0·32	----	
	100·56	100·17	100·00	

I. Analysis by J. Lorenzen, Medd. Groenl., vii, p. 30, 1884.
II. Analysis by H. S. Washington.
III. Analysis II corrected for apatite.
IV. Molecular ratios of III.

There is every reason for the belief that the material analyzed by Lorenzen was essentially identical with that investigated by us, as is also indicated by the agreement in the figures for SiO_2, total iron as FeO, MgO, and CaO, so that the differences between the analyses cannot be ascribed to varying chemical composition. Lorenzen's analysis is seriously defective in the assumption that all the iron is present in the ferrous state, as well as in the non-determination of soda, potash, and water. The last is here of comparatively small moment, but the new analysis shows that about four per cent of alkalies are present, and it is well known that all the basaltic hornblendes and others similar to this contain very notable amounts of soda, with often considerable potash, which cannot be ascribed to inclusions. Lorenzen's figure for TiO_2 is lower than ours by about 3·5 per cent, while his alumina is higher by about the same amount. As our figure for titanium was determined by the colorimetric method, which is capable of a high degree of accuracy, and is the mean of three closely agreeing determinations, we have great confidence in its correctness. It would seem to be highly probable, therefore, that in Lorenzen's analysis part of the TiO_2 was reckoned as Al_2O_3; and this is the more likely as titanium was determined by him by precipitation with sodium thiosulphate, a method which is known to be very uncertain and apt to give either too high or too low results, depending on the amount of acid in the solution and other conditions.

In its general features this analysis much resembles that of the Linosa hornblende, especially in the amounts of silica, alumina, magnesia, lime, and alkalies, as well as in the very high titanium dioxide. The only prominent difference is found in the oxides of iron. The sum of these is considerably higher in the Linosa mineral and the molecular amounts are equal, while in the Kaersut mineral ferrous oxide is largely in excess of ferric, the amount of which is very low.

Interpretation of the Analyses.

The interpretation of the analyses of these two hornblendes in terms of the molecular constitution is rendered subject to grave uncertainty through the presence of the very large amounts of titanium. The uncertainty arises from the fact that this element may be present either as Ti_2O_3 or as TiO_2 or as both oxides together. Potassium permanganate oxidizes Ti_2O_3 to TiO_2 just as it does FeO to Fe_2O_3, so that if the lower oxide of titanium is present it will appear in the ordinary course of analysis as FeO, the apparent amount of which would thus be too high, and that of Fe_2O_3 would be correspondingly low, while the Ti_2O_3 would be determined colorimetrically or gravimetrically as TiO_2.

If all four oxides are or may be present simultaneously, the analytical problem becomes complex and somewhat difficult. A promising line of attack is being developed by Gooch and Newton,* depending on the selective oxidation of the Ti_2O_3 by cupric salts, bismuth oxide, or ferric sulphate, which have no effect on the ferrous oxide. While the results recorded are excellent and show the possibility of very exact estimation under the conditions observed, yet it is uncertain if the methods are applicable, at least without modification, to the analysis of silicate rocks and minerals, owing to their insolubility except in hot hydrofluoric acid and the very ready oxidizability of the hot solutions of Ti_2O_3 and FeO so obtained. It may be suggested that the addition of cupric sulphate to the mixture of hydrofluoric and sulphuric acids employed in determining

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* Gooch and Newton, this Journal, xxiii, 1907, p. 365; H. D. Newton, this Journal, xxv, 1908, pp. 130 and 343. See also G. Gallo, Chem. Zeitung, 1907, p. 399, and A. Cathrein, Zeitschr. Kryst., vi, 1882, p. 248.

FeO might solve the problem. If under such conditions the cupric salt would oxidize the Ti_2O_3 without acting on the FeO, titration with permanganate of two portions brought into solution both with and without the addition of $CuSO_4$, together with the determination of total iron as Fe_2O_3 and of total titanium as TiO_2 by the usual methods, would furnish all the data needed. The discovery of some such method capable of yielding accurate results under the conditions of silicate analysis is now one of the most important desiderata.

In this connection a peculiarity in the relations of the oxides of iron and titanium may be pointed out. In whole numbers the molecular weights are as follows: $Fe_2O_3 = 160$, $FeO = 72$ ($2FeO = 144$), $TiO_2 = 80$ ($2TiO_2 = 160$), $Ti_2O_3 = 144$. That is, neglecting the refinement of decimals, a molecule of ferric oxide is equal to two of titanium dioxide, and one of titanium sesquioxide is equal to two of ferrous oxide. Therefore, to oxidize either FeO to Fe_2O_3 or Ti_2O_3 to TiO_2, one atom of oxygen, equivalent to one-ninth of the lower oxide, will be needed; while conversely, in the case of reduction of Fe_2O_3 to FeO or TiO_2 to Ti_2O_3, one atom of oxygen, equivalent to one-tenth of the weight of the higher oxide, will be subtracted. Exactly the same amount of potassium permanganate, therefore, will oxidize the same weights of iron as ferrous oxide or titanium as sesquioxide to the higher form, as is expressed by the two equations:

$$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O,$$

$$5Ti_2(SO_4)_3 + K_2Mn_2O_8 + 8H_2SO_4 = 10Ti(SO_4)_2 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Fe_2O_3 and $2TiO_2$ on the one hand, and $2FeO$ and Ti_2O_3 on the other, are mutually interchangeable and equivalent as regards titration by permanganate or other such oxidizing aentg. From this it follows that, if Ti_2O_3 is present and the ferrous iron is determined in the usual way, a percentage amount equal to that of the Ti_2O_3 must be deducted from the apparent value for FeO, while an equivalent amount must be added to the apparent amount of Fe_2O_3, and deducted from that of TiO_2.

In the case of minerals whose formulas are simple and well established, readjustment may be made with a fair degree of confidence as to probable correctness, even in the absence of determinations of all four oxides. Such readjustments based on the empirical formula would have still greater weight could it be assumed that ferrous oxide is absent or present in only negligible amounts. This consideration applies to the composition of schorlomite, which we are justified in referring to the garnet group as suggested by Rammelsberg* and discussed in detail by Koenig,† in which enough of the apparent TiO_2 is calculated as Ti_2O_3 to conform to the garnet formula. The case of the hornblendes offers more difficulties, since their molecular constitution is not well understood at present, and is undoubtedly very complex, as is well known.

In a recent important paper, Penfield‡ and Stanley explain the presence of the sesquioxides by "their introduction into the metasilicate molecule in the form of various basic, bivalent radicals," the mass effect of the very complex amphibole acid exerting a controlling influence on the crystal form and other physical characters. They also suggest the possibility that the molecule of the amphibole acid has a ring form, analogous to that of the benzene compounds. By assuming various bivalent radicals, composed of R_2O_3 with F, HO, Na, and R″, which combine with SiO_2 in the ratio of 1:1, a final residue of (Mg, Fe)O and CaO is left which conforms to the same metasilicate ratio. As regards tremolite and actinolite their exact ratios show that the molecule $Na_2Al_2Si_4O_{12}$, suggested by Tschermak, cannot be present, as this would "deplete the total silica and destroy the 1 : 1 ratio." In their calculations of their analyses of the aluminous hornblendes this molecule was also neglected, and very exact metasilicate ratios were obtained without the assumption of its presence. As this paper is the latest and one of the most suggestive and illuminating contributions to our knowledge of the constitution of the amphiboles, a study of our two minerals in its light will be of interest.

The two analyses made by me yield the following ratios, MnO and NiO being reckoned in with FeO :

	Linosa.			Kaersut.		
SiO_2	·681		·787	·659		·788
TiO_2	·106			·129		
Al_2O_3	·097		·153	·110		·118
Fe_2O_3	·056			·008		
FeO	·058	·370	·643	·123	·456	·743
MgO	·312			·333		
CaO	·217	·217		·195	·195	
Na_2O	·032	·039		·048	·059	
K_2O	·007			·011		
H_2O	·010	·017		·033	·033	
F_2	·007					

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* C. Rammelsberg, Min. Chem., 1875.

† G. A. Koenig, Proc. Acad. Sci., Phila., 1886, p. 354.

‡ This Journal, vol. xxiii, p. 23, 1907.

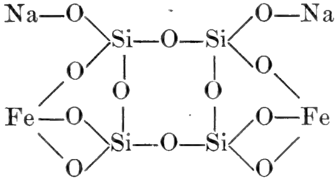
In both cases the ratio of $(Si, Ti)O_2$ to $(R'_2, R'')O$ is greater than unity, being 1·22 in the Linosa, and 1·06 in the Kaersut hornblende. Such relations differ widely from those presented by the hornblendes analyzed by Penfield and Stanley, in which, where the ratio differs notably from unity, it is always on the side of an excess of RO over SiO_2.

Assuming first that all the titanium is present as the dioxide, if we calculate the composition of the molecules in terms of the bivalent radicals suggested by Penfield and Stanley, we obtain residues of SiO_2, (Mg, Fe)O, and CaO, which differ widely from the metasilicate ratio $SiO_2 : RO = 1 : 1$, in that the original excess of silica is here greatly accentuated. This is shown in the table below.

	Linosa.		Kaersut.	
$[(Al, Fe)_2O(F, OH)_2]\ SiO_3$	·017		·033	
$[(Al, Fe)_2O_4RNa_2]\ SiO_3$	·039		·059	
$[(Al, Fe)_2O_3R]\ SiO_3$	·097		·026	
(Mg, Fe)O	·234	·451	·370	·565
CaO	·217		·195	
Residual SiO_2		·634		·670

If, on the other hand, we assume that some of the titanium is present as sesquioxide, by making the necessary calculations and readjustments (the results of which it is needless to give here), we find that this will increase still more the ratio $SiO_2 : RO$, in spite of the reduction in the amount of RO_2, through the diminution in the amount of FeO and the taking up of MgO to form one of the complex radicals. We may therefore assume that all the titanium is present as TiO_2, as this shows less divergence from metasilicate ratios.

It is therefore evident that, for our hornblendes at least, the presence of some other bases or radicals must be assumed, which will take up this seeming excess of silica and at the same time conform to the metasilicate ratio $SiO_2 : RO = 1 : 1$. Such may be found in the molecule $Na(Fe, Al)Si_2O_6$, which exists as the ferric or alumina extreme respectively in riebeckite and glaucophane, and whose presence in many amphiboles was suggested by Tschermak, though not found essential to the interpretation of the hornblendes studied by Penfield and Stanley. This, and the analogous $(Mg, Fe)(Fe, Al)_2Si_4O_{12}$, conform to the normal metasilicate ratio, owing to the trivalence of the basic iron and aluminum; and the molecules may be expressed graphically as ring formulas, quite analogous to those suggested by Penfield, as is shown by that of riebeckite, as follows:



If we assume then the presence of the bases Na_2O and $(Fe,Al)_2O_3$, which will form the metasilicates Na_2SiO_3 and $(Fe,Al)_2Si_3O_9$ respectively, the composition of our amphiboles may be calculated as follows, the presence of some of Penfield's radicals being needed to account for the F and H_2O and the excess of R_2O_3 over the alkalies. The distribution can be made mathematically, so that the whole will conform to the metasilicate formula, by the use of equations analogous to those used in the calculation of the norms of igneous rocks.*

	Linosa.		Kaersut.	
$[(Al, Fe)_2O_3(F, OH)_2]\ SiO_3$	·017		·033	
$[(Al, Fe)_2O_3R]\ SiO_3$	·088		·026	
$[(Al, Fe)_2O_3Na_2]\ SiO_3$	----		·044	
$Na(Al, Fe)Si_2O_6$	·039		·015	
$(Mg, Fe)\ (Al, Fe)_2Si_4O_{12}$	·009		----	
$(Mg, Fe)O$	·273	·490	·429	·624
CaO	·217		·195	
Residual SiO_2	----	·490	----	·625

Assuming that the amphiboles are metasilicates, as is held by most authorities, and which view is greatly strengthened by the work of Penfield and Stanley, it is clear that the composition of the hornblendes of Linosa and Kaersut may be rationally explained by the assumption of the presence of molecules of the general type $(R'_2, R'')\ R'''_2\ Si_4O_{12}$. The presence of these molecules also seems to be quite unavoidable in the case of such amphiboles as riebeckite and glaucophane, and furthermore they cannot be interpreted only in terms of bivalent radicals such as those suggested by Penfield and Stanley, though some of these may be assumed to be present.

The two authors mentioned do not discuss the question of the presence of such riebeckitic molecules, an omission unhesitatingly to be ascribed to the preliminary and, most sadly, unfinished character of their paper. Such a discussion would have been inevitable had their investigation been extended to the glaucophanes, riebeckites, and other highly sodic amphiboles, as one of us knows to have been the late Professor Penfield's intention. So far as can be learned from the published

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* Cross, Iddings, Pirsson, and Washington, Quantitative Classification of Igneous Rocks, Chicago, 1903, pp. 194, 195.

paper their objection to the introduction of the molecule under discussion lay in the fact that, according to Tschermak's theory, "a definite basic alumo-silicate molecule is regarded as isomorphous with Ca (Fe, Mg)$_3$Si$_4$O$_{12}$."* As has been shown above, however, such a riebeckite-glaucophane molecule may be regarded as a metasilicate and may be written structurally as a ring formula, exactly analogous to those suggested by the authors named. It is clear, therefore, that the presence of a riebeckitic molecule need not be regarded as a case of isomorphism of two chemically and structurally unlike molecules, or as inconsistent with the views of Penfield as to the structure of the amphibole acid and the mass effect of complex mineral molecules. On the contrary, they are in complete accord, as the matter reduces itself, in the last analysis, to the simultaneous replacement of one hydrogen atom by Na and three by Fe$'''$, just as two atoms are replaced by Ca$''$, (Mg, Fe)$''$, or by one of Penfield and Stanley's bivalent radicals.

These authors noted the highly interesting and probably significant fact that the CaO formed "very closely 25 per cent of the various radicals and bases, or in other words replaces one-fourth of the hydrogen atoms of the amphibole acid." Without giving all the percentage figures, in the Linosa hornblende, as calculated above, CaO forms 33·8 per cent, and in that of Kaersut 26·3 per cent. The latter approximates to one-quarter, while the former is about one-third of the radicals and bases. If this last is substantiated by analyses of other hornblendes, and found to be characteristic of certain kinds, it might be held to indicate that the amphibole acid contains a number of hydrogen atoms which is divisible both by 4 and by 3, such as $H_{12}Si_6O_{18}$, or a multiple of this. But our data are at present far too insufficient for more than a speculative suggestion.

As is well known, the amphiboles which are high in soda and in alumina or ferric oxide, and which there is good reason to believe contain the riebeckite-glaucophane molecule or basic (Al,Fe)$'''$, such as riebeckite, glaucophane, arfvedsonite, crossite, hastingsite, barkevikite, aenigmatite, and those we have been describing, are all intensely pleochroic and show either very distinctive blue colors or very intense reds and browns. Similarly, the pyroxenes which contain the acmite molecule, or basic Na$'$ and (Al,Fe)$'''$, as aegirite, aegirite-augite, babingtonite, etc., are deeply colored and are characteristically pleochroic, in contrast with the common, generally non-pleochroic pyroxenes, which do not contain the acmite molecule. On the other hand, the amphiboles which contain trivalent Al and Fe only in bivalent radicals, on the theory of

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* Penfield and Stanley, op. cit., p. 49.

Penfield and Stanley, as actinolite or common hornblende, are less deeply colored, are never blue, and are markedly less pleochroic ; and the same is true of the ordinary pyroxenes and augites.

It is commonly supposed* that the blue color of these amphiboles is connected with the presence of abundant iron, and Pirsson† has recently suggested that the blue color is due to the presence of ferrous-ferric molecules, the analogy of Prussian blue and altered vivianite being cited. Since, however, a similar color is characteristic of glaucophane and gastaldite, in which the trivalent element is practically entirely aluminum, ferric iron being either absent or present in small amount, it would seem to be necessary to amend this hypothesis by assuming aluminum to replace the ferric iron either wholly or partially. Similarly the deep browns and reds are supposed to be connected with the presence of titanium and, as pointed out by Brögger,‡ the intensity of the color increases with increasing content in this element, as is shown by the series barkevikite, basaltic hornblende, and kaersutite and aenigmatite.

We have seen above that $(Al, Fe)'''$ may enter the amphibole molecule either in a bivalent radical, such as those suggested by Penfield and Stanley, the radical as a whole acting as a base, or it may itself act as a base, replacing three atoms of hydrogen in the amphibole acid. It would thus occupy different positions and perform very distinct functions in the molecular arrangement. In these different positions, therefore, the trivalent element may reasonably be supposed to affect differently the optical and other physical properties of the minerals into which it enters, in analogy with the well-established fact in the chemistry of the carbon compounds.

Following out this line of thought, it may be suggested that this basic $(Al, Fe)'''$, and not that which forms part of bivalent radicals, acts as a chromophore, as such color-giving radicals are known in organic chemistry, where they are especially notable among the aromatic compounds; and that, furthermore, the property of pleochroism may be connected with its presence, this either causing a mineral variety to be absolutely pleochroic, when varieties in which the basic trivalent element is not present are not so, or intensifying the pleochroism of otherwise weakly-pleochroic complex mineral molecules. That this chromophoric radical does not consist solely of $(Al, F)'''$, but contains Na as well, probably in the ratio 1 : 1, is indicated by the constant presence of much soda in the peculiarly colored and pleochroic amphiboles and pyrox-

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*Cf. W. C. Brögger, Grorudit-Tinguait Serie, p. 35, 1894.

†L. V. Pirsson, this Journal, vol. xxiii, p. 440, 1907.

‡Brögger, loc. cit.

enes which are under discussion, as well as by the fact that these constituents generally show such a constant ratio, as pointed out by Doelter.* The partial replacement of Na_2 by (Fe, Mg)″, sometimes observed, would harmonize this idea with that of Pirsson.

The chromophoric titaniferous radical would seem to be more intensely active or color-producing than the alumo-ferric-soda one, since amphiboles high in titanium, but otherwise chemically like those low in this element, are red-brown rather than blue, as is shown by the relations of aenigmatite and arfvedsonite. But its nature is at present difficult to suggest. The ability of titanium to assume some seven states of oxidation† complicates the problem immensely, even though this possible number is lessened by considering only the oxides most commonly met with, Ti_2O_3, TiO_2, TiO_3. It may only be mentioned here that the violet or blue colors of solutions of Ti_2O_3, and the yellows and deep browns of those containing TiO_3,‡ such as are produced from colorless TiO_2 solutions on the one hand by reduction with zinc or tin, and on the other by the action of H_2O_2, may be possibly significant of the condition of oxidation of the titanium.

The constant, characteristic pleochroism of the colored, common amphiboles, which do not contain the supposedly chromophoric Na (Al, Fe)‴ radical, as contrasted with the equally characteristic non-pleochroism of the colored, common pyroxenes (free from the acmite molecule), leads also to the speculative suggestion that the difference is possibly connected with difference in the structure of the molecule. Accepting provisionally the suggestion of Penfield and Stanley that the amphibole acid has a closed chain or ring structure, it might be advanced as possible or probable, in analogy with the carbon compounds, that the pyroxene acid is of the open chain type. Or the relations might be the reverse.§

In our present state of complete ignorance as to the constitution and structure of the mineral molecules any such suggestion as is here made can but be regarded as a hypothesis of the most speculative character. But such a difference in structure would be a fundamental one between the molecules of the pyroxenes and the amphiboles, and it undoubtedly exerts a profound influence on the physical properties of isomers, as the pyroxenes and amphiboles are regarded with reason as being.

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* C. Doelter, Zeitschr. Kryst., vol. iv, p. 40, 1880.

† P. E. Browning, Introduction to the Rarer Elements, p. 61, 1903.

‡ A. Classen, Ausgew. Methoden Anal. Chem., vol. i, p. 765, 1901.

§ It is, of course, understood that the terms "open chain" and "closed chain" are used as they are in organic chemistry, without implying that they actually thus represent the structure of the molecule, or the arrangement of the atoms in space.

It might explain the inconsistency of the apparently greater chemical complexity and hence probably greater molecular weight of the amphiboles, as suggested by Tschermak, and the higher specific gravity of the pyroxenes, which Clarke* urges as evidence of their greater molecular weight. It might also readily explain the characteristic difference in pleochroism between the two groups noted above.

In this connection the analogy of the carbon compounds is of interest. The greater part of these are referred, as is well known, to two great groups; the aliphatic compounds, derivatives of methane, with an open chain type of formula; and the aromatic compounds, derivatives of benzene, with a closed chain type of formula. These two groups show characteristic differences in general chemical behavior, and also characteristic differences in some physical properties. Thus, the aliphatic compounds are very rarely colored, while colored compounds are quite common among the aromatic bodies. Similarly solutions of members of the first group seldom show absorption bands, while those of the other, when colorless, often do so.

The analogy cannot, of course, be pushed very far, but that such a fundamental difference in molecular structure would not be inconsistent with the alteration of amphibole to pyroxene, or the converse change of pyroxene to uralite, is indicated by the convertibility of members of the aliphatic series into those of the aromatic series, and vice versa. It may furthermore be observed that very many organic compounds are known which contain radicals belonging to both series, such as toluene (methyl-benzene), $C_6H_5.CH_3$, and such pyroxenes as aegirite-augite might be regarded as possible analogues.

Correlation and Name.—In the annexed table are given analyses of several hornblendes which resemble those of Linosa and Kaersut in one feature or another. In their general characters, on the whole, these most approach the basaltic hornblendes, or syntagmatites, as Rosenbush has recently proposed that these should be called,† especially in the figures for silica, iron oxides, magnesia, lime, soda, and potash. The alumina of our minerals is distinctly lower than in these, but the figures for this constituent in analyses of the syntagmatites (in this sense) are somewhat discordant. That shown in III is very high, while the analyses of Schneider run rather uniformly between about 14 and about 15. Also TiO_2 is much higher in I and II than in the syntagmatite analyses. The analysis (III) of a typical "basaltic hornblende" shows but little TiO_2, much less than in the analyses of Schneider (cf. IV and VI), where it varies from 4·26 to 5·40. The correct-

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* F. W. Clarke, Bull. No. 125 U. S. Geol. Surv., p. 90, 1895.

† H. Rosenbusch, Mikr. Phys., vol. i, 2d half, 1905, p. 236.

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
SiO_2	40·85	39·52	39·95	39·75	39·66	40·15	42·46	34·18	43·85	37·92	43·55	24·42
TiO_2	8·47	10·31	1·68	5·40	0·89	5·21	----	1·53	----	7·57	----	9·46
Al_2O_3	9·89	11·22	17·58	15·00	14·83	14·34	11·45	11·52	4·45	3·23	4·96	17·25
Fe_2O_3	8·85	1·22	7·25	7·86	12·37	7·80	6·18	12·62	3·80	5·81	7·97	11·69
FeO	3·96	8·81	2·18	2·89	1·97	4·53	19·93	21·98	33·43	35·88	32.87	11·39
MnO	0·12	0·06	tr.	----	----	----	0·75	0·63	0·45	1·00	1·98	----
NiO	0·10	none	----	----	----	----	----	----	----	----	{ CuO 0·39 }	----
MgO	12·47	13·31	14·15	14·16	14·25	13·14	1·11	1·35	0·81	0·33	0·86	12·62
CaO	12·16	10·93	11·96	12·97	12·74	11·75	10·24	9·87	4·65	1·36	2·01	12·43
Na_2O	2·01	2·95	3·16	1·92	2·47	2·31	6·08	3·29	8·15	6·58	5·29	0·67
K_2O	0·63	1·07	1·98	1·61	1·25	1·14	1·44	2·29	1·06	0·51	0·33	0·63
H_2O	0·19	0·59	0·41	----	----	----	----	0·35	0·15	----	----	----
F_2	0·28	----	0·03	----	----	----	----	----	----	----	----	----
	99·98	100·00	100·46	101·56	100·43	100·37	99·64	99·61	100·80	100·19	100·21	100·56

I. Kaersutite. Monte Rosso, Linosa. Washington analyst.

II. Kaersutite. Kaersut, Greenland. Washington analyst.

III. Syntagmatite (basaltic hornblende). Bilin, Bohemia. Stanley analyst. This Journal, xxiii, 1907, p. 40. (Includes 0·13 loss at 110°.)

IV. Syntagmatite (basaltic hornblende). Bohemia. Schneider analyst. Zeitschr. Kryst., xviii, 1890, p. 580.

V. Syntagmatite (basaltic hornblende). Bohemia. Schmidt analyst. Tsch. Min. Pet. Mitth., iv, 1881, p. 23.

VI. Syntagmatite (basaltic hornblende). Härtlingen, Westerwald. Schneider analyst. Zeitschr. Kryst., xvlii, 1890, p. 580.

VII. Barkevikite. Barkevik, Norway. Flink analyst. Zeitschr. Kryst., xvi, 1890, p. 412.

VIII. Hastingsite. Dungannon, Ontario. Harrington analyst. This Journal, i, 1896, p. 210.

IX. Arfvedsonite, Kangerdluarsuk, Greenland. Lorenzen analyst. Min. Mag., v, 1882, p. 50.

X. Aenigmatite. Naujakasik, Greenland. Forsberg analyst. Zeitschr. Kryst., xvi, 1890, p. 428.

XI. Cossyrite (aenigmatite). Pantelleria. Foerstner analyst. Zeitschr. Kryst., v, 1881, p. 354.

XII. Rhönite. Platz, near Brückenau, Rhön. Dittrich analyst. Neues Jahrb., Beil. Bd. xxiv, 1907, p. 498.

ness of the analyses made by Stanley under the direction of so preëminent an analyst as the late Professor Penfield cannot be doubted, and it is not probable that Schneider's figures are seriously in error, especially as he states* that special attention was paid to the determination of this constituent, though he does not mention the method employed.

In passing, a few remarks may be made in regard to Nos. IV and V. The exact localities of these hornblendes are not given by either author, but they both are said to come from Bohemia, and the extremely close similarity in the figures for SiO_2, Al_2O_3, FeO, MgO, CaO, Na_2O, and K_2O makes it probable that they were made on identical amphibole from the same locality. In view of this remarkable agreement of the constituents mentioned, the discrepancies observed in the figures for TiO_2 and Fe_2O_3 are noteworthy. In IV TiO_2 is higher and Fe_2O_3 lower, while in V the reverse is true. The sum of the two in each case is, however, exactly the same, 13·26. The exact agreement is, of course, a coincidence, but taken in connection with the close concordance in the other constituents, and having regard to the methods of analysis, it suggests the explanation that in IV the ferric oxide was determined by reducing the iron by H_2S, which does not act upon TiO_2, while in V the iron was reduced by zinc, which would reduce the TiO_2 to Ti_2O_3, and the latter would appear as Fe_2O_3, after subtraction of the FeO. On this supposition the lower TiO_2 of V, in conjunction with the close agreement between the figures for Al_2O_3, would be explained by the use of the method of boiling an acid solution with SO_2, which is as apt to give too low as too high results, or even possibly by the assumption that the residue left on evaporation of the silica with HF is wholly TiO_2, a not uncommon error, especially in former days. The presumption therefore is that IV represents the true composition more accurately than V. The matter, after all, is of little importance, but serves to illustrate the need of a critical study of analytical data in the light of the methods of analysis.

The blue arfvedsonitic amphiboles (IX) and the triclinic aenigmatite (X and XI) resemble ours in the figures for SiO_2 and K_2O, and especially in the high TiO_2 of the Greenland aenigmatite. TiO_2 was not determined in the analysis of arfvedsonite and the Pantelleria cossyrite, but it is presumably present in both, and almost certainly very abundantly in the cossyrite, as Brogger has shown. Additional reasons for this belief will be given in a forthcoming paper on the rocks of Pantelleria. These hornblendes differ, however, widely from ours in the lower Al_2O_3, the very much higher FeO and Na_2O, and in the very low MgO and CaO. The recently discovered triclinic

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* C. Schneider, Zeitschr. Kryst., vol. xviii, p. 579, 1890.

rhönite (XII) is unique in its low silica, but in other respects resembles our amphiboles more than it does the triclinic aenigmatite, though the Al_2O_3 is remarkably high.

On the whole, therefore, our amphiboles may be considered to belong to the basaltic hornblendes or syntagmatites, rather than to the arfvedsonite group, and this general relationship is confirmed by the color, the etch figures, and the negative extinction angle of the Kaersut mineral. The very high TiO_2, however, places them in a subdivision apart and, with the small positive extinction angle of the Linosa mineral, indicates a transition toward the arfvedsonite group.

On account of their chemical characters, and also because of the position of the negative extinction angles $c \wedge \mathfrak{c}$, barkevikite (VII) and hastingsite (VIII) may also be regarded as transitional between typical syntagmatite and the arfvedsonites, though in the direction opposite to ours. A similar relation is suggested by Brögger,* who regards kaersutite as an end member of the basaltic hornblendes.

The name kaersutite may well be reserved for such highly titaniferous basaltic hornblendes or syntagmatites, and the mineral from Greenland may be regarded as the type. Whether the same name should be applied to the Linosa hornblende or not is somewhat doubtful. The two are chemically closely similar, but show a marked divergence in the relative amounts of the iron oxides. Also the physical characters are alike in nearly all respects. The only differences of note are the somewhat higher specific gravity and indices of refraction of the Linosa mineral, and the difference in the extinction angle, which last would seem to be the more important. Indeed, while that of the Kaersut amphibole is negative and lies well within the limits of the extinction angles shown by the ordinary syntagmatites, that of the Linosa amphibole is close to the vertical axis, but slightly positive, and indeed occupies a unique position between the extinctions of the riebeckite-arfvedsonite group on the one hand and those of the syntagmatites on the other, though it must be remembered that in the former group the bisectrix which lies nearest the vertical axis is $\mathfrak{a}$, not $\mathfrak{c}$. The physical characters of our two minerals are tabulated below.

The Linosa hornblende might be regarded as an end member of the highly titaniferous syntagmatites, in which case the name kaersutite would apply to it, or its peculiar extinction angle, and the high ferric oxide might justify the separation of it from this group as a distinct subspecies, to which the name *linosite* may be given. In view of the uncertainty of our

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* Brögger, Grorudit-Tinguait Serie, p. 35, 1894.

	Linosa.	Kaersut.
Specific gravity	3·336	3·137
Crystal system	monoclinic	monoclinic
$110 \wedge 1\bar{1}0$	55° 22′	55° 35′
$\mathfrak{c} \wedge c$ on 110	+1° 24′	−8° 9′
Optical character	negative	negative
Color	deep brown	chestnut brown
Absorption	$\mathfrak{c}>\mathfrak{b}>\mathfrak{a}$	$\mathfrak{c}>\mathfrak{b}>\mathfrak{a}$
α	1·692	1·676
β	1·731	1·694
γ	1·760	1·708
$\gamma-\alpha$	·068	·032
2V	79° 54′	82° 6′
Dispersion	(?) weak	(?) weak

knowledge of the true chemical composition and relations of the hornblendes, the numerous varieties that are constantly being observed and often named, and the fact that many well-recognized species show greater divergence in physical properties and chemical composition than do our minerals, it seems to us advisable not to bestow a new name at present on the Linosa hornblende, but to consider it a kaersutite.

In conclusion attention may be called to the somewhat remarkable coincidence between the finding of kaersutite both in Greenland and on Linosa, and the similar occurrence of aenigmatite in Greenland and the apparently identical cossyrite on Pantelleria, which lies close to Linosa. In both the Arctic and the Mediterranean localities these minerals occur in comparative abundance and as material which can be easily studied, while elsewhere kaersutite is unknown and aenigmatite very rare and the crystals small and unsatisfactory.

Locust, New Jersey, and
Geophysical Laboratory of the
Carnegie Institution of Washington, D. C.

ART. XXIV.—*The Geology of the Isthmus of Panama*; by ERNEST HOWE.

Introduction.

THE first serious effort to investigate the geology of the Isthmus of Panama was made by Robert T. Hill in 1895.* Although his stay on the isthmus was brief and the survey merely a hurried reconnoissance, the principal features of the geology and physiography were recognized. At the time of his visit little or no work was being done by the French company, few records of borings or soundings were available, and many exposures along recent cuts were already in the grasp of the jungle, so that certain details that escaped Hill remained to be worked out by MM. Bertrand and Zürcher† three years later when they made a report to the New Panama Canal Company. Working under more favorable conditions, these geologists were able to revise certain of Hill's views, and especially his conclusions concerning the igneous rocks.

In the following pages numerous references are made to the reports of Hill and of Bertrand and Zürcher, from which great assistance has been derived in the course of my own studies of the isthmian geology.

The field work upon which the present paper is based was carried on during a part of the summer of 1906, and in the following dry season from January to April, 1907, nearly five months in all. The work was undertaken for the Isthmian Canal Commission and had to do largely with economic matters; a brief outline of the geology, however, accompanied the report to the Canal Commission‡, a résumé of which has been published in "Economic Geology".§

The purpose of the present paper is to record in more detail certain observations on the geology, and more especially on the stratigraphy, that affect the conclusions reached by Hill and the French geologists. There were unusual opportunities for studying the section across the isthmus because of fresh exposures made by recent excavation along the canal line, and

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* Robert T. Hill, The Geological History of the Isthmus of Panama and Portions of Costa Rica. Bull. Museum. Comp. Zool., vol. xxviii, No. 5, pp. 149–285. Cambridge, 1898.

† M. Bertrand and P. Zürcher, Étude Géologique sur l'Isthme de Panamá. Rapport de la Commission. Compagnie Nouvelle du Canal de Panamá, etc. Annexe I, pp. 85–120. Paris, 1899. The page references in the present paper are to a reprint of this report.

‡ Ernest Howe, Report on the Geology of the Canal Zone, Annual Rep. Isthmian Canal Commission, 1907. Appendix E, pp. 108–138.

§ ——— Isthmian Geology and the Panama Canal, Economic Geology, vol. ii, pp. 639–658. 1907.

at many places the information to be obtained from surface outcrops was augmented by a great number of boring records and samples.

Special thanks are due Mr. John F. Stevens, under whom as chief engineer the work was done, for many facilities placed at my disposal. I am also greatly indebted to Dr. William H. Dall for his kindness in looking over my collections and for many valuable suggestions.

Preliminary Statement.

The Isthmus of Panama, where it is to be crossed by the canal, consists of sediments and pyroclastics of Tertiary age that rest on an eroded surface of andesitic breccias and associated lava flows, all of which have been intruded at numerous places, probably in Miocene time, by dikes and large cross-cutting masses of andesite or basalt. During the period of intrusion, or immediately after it, the region was uplifted, and the cycle of erosion thus inaugurated continued to late maturity or old age. Before the completion of the cycle, however, another upward movement occurred accompanied by warping or a gentle medial doming. As a result of the continued erosion the basal igneous mass was exposed in the interior and a sub-mature topography developed in regions of harder rocks, while near both coasts less resistant sedimentary beds favored more active erosion and conditions of greater maturity prevailed. A third uplift caused the streams to entrench themselves in their old or mature valleys, but before this last cycle had advanced beyond its youth, a gradual subsidence began that continued until the young valleys were aggraded and the mature valleys of the second cycle drowned for short distances back from the coasts. A final slight upward movement has elevated the estuarine deposits, formed during the period of depression, a few feet above sea level.

Obispo Breccias.

The igneous complex that appears to underlie all of the other formations of the isthmian region consists largely of andesitic tuffs and breccias; it has been given the name Obispo on account of its characteristic exposures at Bas Obispo, the northern end of the Culebra cut. From Bas Obispo southward to a point between Empire and Culebra the breccias have been well exposed by excavation, but at the time of examination the zone of surface alteration had not been passed, so that although the rocks show their pyroclastic nature the petrographical character of the fragments and the matrix is not readily determinable. Fresher material was collected on the

Pacific side of the isthmus in the vicinity of Las Sabanas, and this has been compared with specimens from the other localities which seem to be equivalent.

The formation as a whole consists of moderately coarse breccias of andesite of a variety of textures but nearly uniform composition. Fine-grained tuffs have been observed, mostly on the northern side of the isthmus, while the Sabanas occurrences present an extremely coarse facies. As a rule the breccias of the interior are composed of angular fragments varying from a quarter of an inch to two inches in diameter. At a quarry near the Sabanas road one block more than six feet in diameter and many twelve or eighteen inches in diameter were observed in a cement as coarse as the average breccia of the interior. In a region where outcrops are few and continuous exposures unknown it is not possible to make generalizations, but from the observed occurrences it may be said that the usual appearance of the Obispo breccia lies between the extremes of coarseness and fineness that have been mentioned.

So far as observations have been carried, the rock fragments composing the breccias consist largely if not entirely of pyroxene-andesite. Some are highly vesicular and glassy, others markedly porphyritic, while the majority are dense, even-textured rocks in which individual crystals can be made out only with the aid of a lens. In one specimen there were doubtful indications of hornblende. The prevailing greenish gray color of the rock suggests what is found to be the case on microscopical examination, that the pyroxene, usually augite, has undergone extensive alteration; on the other hand, the plagioclase, which generally has a composition of about Ab_2An_3, is comparatively fresh, a fact noted in the cases of most of the rocks of the isthmus where the final stage in the decomposition to the surface red clay has not set in.

Distribution of the Obispo breccia.—The most northerly occurrences of these breccias are shown by borings at the San Pablo dam site; from that point southward they appear occasionally at the surface, and are indicated in all the borings made at intervals of one kilometer along the center line of the canal as far as Empire. Decomposed but otherwise characteristic exposures are to be seen between Mamei and Gorgona along the Panama Railroad, and from Gorgona to Empire, where they disappear beneath a cover of later sediments, the Obispo breccias are the prevailing rocks. Composing the hills north, west, and east of Corozal, and particularly well exposed northeast of Panama in the vicinity of Las Sabanas, are rocks of the same petrographical character that are believed to be a part of the central mass.

Age of the Obispo breccias.—The only definite statement that can be made in regard to the age of the Obispo breccias is that they are older than the oldest sedimentary rocks of the region, which, as will be shown presently, carry a fauna considered by Prof. William H. Dall to correspond to the Claiborne Eocene. Although it is not improbable that the eruption of these andesitic breccias marked the beginning of Tertiary history in the isthmian region, there is no direct evidence that the rocks are not still older.

MM. Bertrand and Zürcher* included with the breccias that have been described as the Obispo, certain other fragmental igneous rocks exposed near Bohio, calling the whole "Roche de Gamboa." From fossil evidence found at Bohio they correlated the Gamboa rock with the Oligocene of southern Europe. Reasons are given in a later paragraph for believing that the breccias at Bohio are intimately associated with the oldest sedimentary rocks and separated from the Obispo breccias by an unconformity.

Bohio Formation.

The name Bohio is proposed for the oldest sedimentary formation recognized on the isthmus and includes certain beds occurring at Bohio, Vamos Vamos, and in the vicinity of Gatun. This name is suggested in order to avoid confusion in referring to the same rocks described by Hill and Bertrand, but not recognized by them as being parts of one formation.

What are believed to be the lowest beds of this formation are conglomerates exposed in the lock site partly excavated by the French near Bohio, and breccias in the quarries at the Bohio railway station. A mile and a half to the west, at a locality known as Vamos Vamos, rocks of the same age are exposed on the south bank of the French canal, and similar rocks, although no fossils have been found among them, occur along the Panama Railroad near Tiger Hill. On the west bank of the canal nearly opposite the mouth of the Gatuncillo the formation is again exposed and the beds carry abundant fossils. At intermediate points borings have shown the presence of rocks lithologically the same as those at Vamos Vamos or near Gatun, but their few fossils have been indeterminable. To the southeast of Bohio borings in the vicinity of Buena Vista and San Pablo have indicated the presence of beds like those at Bohio, while a few isolated patches of conglomerate that rest on the Obispo breccias in the neighborhood of Mamei, Gorgona, and Matachin, are in all probability a part of the Bohio formation.

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* Étude Géologique sur L'Isthme de Panama, p. 5.

Lithologic character of the Bohio rocks.—Lack of continuous outcrops and sudden changes in the character of the beds within short distances have prevented an altogether satisfactory study of the Bohio formation. Boring records have assisted at a number of places, but even with their help the relations at Bohio are not easy to make out.

Directly south of the village of Bohio on the opposite side of the river is a hill about seventy-five feet in elevation, through the middle of which a cut was made by the French for the construction of a lock. The sides of the cut are now more or less covered by vegetation but still present excellent exposures of the rocks composing the hill. The section shown is about fifty feet in thickness and consists of beds of coarse conglomerates, gravels, and sands that strike N. 25° E. and dip about 14° to the northwest. Crossbedding is common and the beds of finer textured rocks are frequently lenticular. The conglomerates contain many bowlders a foot or more in diameter associated with coarse gravel or cobbles and held in a gritty matrix that is of the same character as the beds of finer sandstone. The bowlders are of a number of kinds of eruptive rock, the commonest being hornblende-andesites with less abundant hornblende augite-andesite, augite-andesite and latite porphyry; nearly all are coarse-grained and strongly porphyritic. It is noteworthy that of the bowlders examined few resembled rocks observed in other parts of the isthmus. The matrix in which these bowlders lie and the associated sandstones are composed of finer debris of the same rocks; quartz is so rarely present as to be negligible. It is worth noting in this connection that the bowlders of the conglomerate are of comparatively fresh rock while the matrix and intercalated sandstones are invariably decomposed, the alteration being to a complex aggregation of epidote, serpentine, kaolinite and sericite that causes the rocks to have a distinctly soapy feel. This is a feature common to most of the fragmental rocks not of direct volcanic origin, wherever alteration has not progressed so far as to result in the formation of the surface red clays.

Not more than a quarter of a mile north of the conglomerates exposed at the Bohio lock site, outcrops of a peculiar greenish brown rock are to be seen on the right bank of the Chagres beneath the village of Bohio. The hills to the north and east are composed of the same rock, and just back of the village, quarries are located from which building stone has been obtained for the Panama Railroad bridge piers and other purposes. The quarrying operations have exposed a vertical section of the rock about fifty feet thick. The rock is composed of fragmental materials of volcanic origin; the imbedded fragments are largely of pyroxene-andesite of a number of different textures, often fluidal and glassy, and varying from a tenth of an inch to one or two inches in diameter. Although many of the fragments are comparatively fresh, the matrix or cement is in an advanced state of decomposition, the secondary minerals being zoisite, epidote, serpentine, and some doubtful kaolinite. As a whole, however, the rock is so extremely altered that it is difficult to determine whether it is a simple volcanic breccia like the Obispo or a fine conglomerate of volcanic debris like that at the near-by lock site. So far as it is possible to make out, I am inclined to believe that it is a volcanic breccia, in the sense that it is more or less of eruptive origin, largely on account of the uniform character of the rock fragments composing it as contrasted with the varied petrographic character of the bowlders in the conglomerate at the lock site. It is not impossible that the breccia represents a "volcanic mud-flow" as suggested by Bertrand.*

The particular interest attaching to this breccia is its intimate association with the conglomerates exposed at the lock site. This relation is not shown on the surface, but is brought out very clearly by borings made in exploring possible dam sites in the vicinity. One series of these borings, along what is known in the surveys as the "F" line, extended from the quarries at Bohio in a southerly direction across the river to the hill through which the French excavated the lock site, a distance of about one-half mile. At the northern and southern ends of this line respectively characteristic specimens of the breccia and of the conglomerate were obtained by the drill, while at intermediate points transitional facies were shown in nearly all the borings. Among other features is the association of the typical breccia of the quarry with water-laid sandstones or tuffs, many of which contain carbonaceous matter, while others, coarser grained, are composed of distinctly water-worn material and are held in a calcareous cement. Passing southward the breccias become less and less abundant while the water-worn material increases in coarseness and conglomeratic beds are to be noted in many of the holes. Layers of fine material interbedded with both the typical breccia and with the coarse conglomerates, as at the French lock site, are shown in practically all the borings.

The lowest point reached by the drills was about 194 feet below sea level near the middle of the line of borings. After passing through alluvium filling the Pleistocene valley of the Chagres, the deepest boring entered about thirty feet of coarse conglomerate; the matrix holding the bowlders was ground up by the drill and none is shown in the samples collected, but

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* Op. cit., p. 5.

the presence of certain porphyritic rocks closely resembling those contained in the conglomerate of the lock site makes me believe that this is to be regarded as a conglomerate rather than as a breccia like that of the quarry where little or no variation in the character of the fragments of pyroxene-andesite was found. One hundred feet south of this point another boring passed through fine sandstones or tuffs before striking beds similar to those in the previous hole and at a corresponding elevation. About the same distance to the north from the first hole and at the same elevation, fine-grained beds like those of the second hole are also shown by the core, while still nearer the quarries and at an interval again of about one hundred feet fine material mixed with angular fragments of pyroxene and andesite is shown. In the opposite direction a corresponding change to the conglomerate facies is to be observed. Precisely the same transition is shown by a line of borings made from the hill in which the French lock site was excavated in a northeasterly direction across the valley of the Chagres to the hills east of Bohio.

This evidence would seem to indicate that the breccias, best shown at the quarries, were deposited contemporaneously with the conglomerates and sandstones of the lock site. The breccias were in large part, if not entirely, laid down in water, and probably running water, but it is impossible to decide whether the material composing the breccia was transported for some distance by streams before being deposited or if it fell into the water directly from the air. The angular character of the fragments, so far as it may be determined in the extremely decomposed rock, would seem to favor the direct deposition of the breccia in water as a result of volcanic eruption. Eruptions of fragmental material of uniform composition undoubtedly took place during this first period sedimentation, and evidence for this has been found at other points, especially in the vicinity of Culebra, as stated in a later paragraph.

Southeast of Bohio the character and distribution of the conglomerates and breccias are imperfectly known. Near San Pablo rocks similar to the Bohio breccias are indicated by borings beneath acid tuffs, while it is more than probable that the Bohio beds are represented in the neighborhood of Gorgona by conglomerates exposed along the line of the Panama Railroad. In most instances it is all but impossible to distinguish between the conglomerates and the volcanic breccias upon which they rest because of the extreme decomposition that both have suffered. The occurrences at Gorgona are fresher, however, and their conglomeratic character unmistakable. The andesitic breccias beneath these conglomerates belong to the Obispo formation and have been traced by borings practically all the way from near San Pablo to the type locality at Bas Obispo. Hill noted the presence of these conglomerates at the places named and correlated them with the beds at the Bohio lock site.*

Vamos Vamos and Gatun beds.—About two and a half miles west of Bohio, on the south bank of the French canal, at a locality known as Vamos Vamos, are exposures of sedimentary rock that have been described by Hill† and Bertrand.‡ The rocks are impure calcareous shales or marls of a dirty brown color, rich in fossils, and at certain horizons contain numerous large fossiliferous calcareous concretions that at first suggest bowlders in a conglomerate.

Following the line of the French canal northwest for nearly six miles, no outcrops of any sort are to be seen until within a short distance of Gatun, where, on the left bank of the canal, are exposures of extremely fossiliferous marls and calcareous sandstones. Similar beds are exposed along the cuttings of the Panama Railroad through Tiger Hill between Bohio and Gatun. No other exposures in this region are known, but a great number of borings made at Gatun in exploration of dam and lock sites furnish much valuable imformation in regard to the character of the rocks. The samples of borings from the lowest sedimentary rocks at Gatun are all of extremely fine-grained, even-textured sandstones which in some places merge into sandy shales. The cementing material is usually calcareous, but considerable earthy impurity or clay is often present. The coarser components of the rock at Gatun and of that occurring along the canal between Gatun and Bohio consist of igneous material; in many specimens grains of nearly fresh feldspar and ferro-magnesian silicates may be recognized, but as a rule the material is in such a finely divided state that it is impossible to say whether it is of direct volcanic origin or has resulted from the degradation of older igneous rocks. At many points fossils are abundant in the core specimens and carbonaceous matter is very generally present.

Age of the Bohio formation.—From fossils collected by Hill and others and by myself and examined by Dr. William H. Dall, it appears that the beds described are of Eocene age and contain a number of species typical of the Claiborne and some common to the Upper Tejon of California.§ In the material that I collected at Vamos Vamos Dall has identified the following species:

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* Op. cit., 188. † Op. cit., p. 179. ‡ Op. cit., p. 6.

§ Hill, op. cit., Part VI, Report by Dr. William H. Dall upon the Paleontology of the collections, pp. 271–275.

Lupia perovata Conr.
Glyptostyla panamensis Dall.
Turritella gatunensis Conr.
Marginella sp.
Natica (cf. *eminula* Conr.)
Pleurostoma sp.
Dentalium sp.
Cytherea
Mactra
Corbula
Tellina
Leda sp.
Pyramidella sp.

In addition to these there are fragments of *Ostrea* sp., *Liocardium*, and *Pecten*, and a small ribbed *Cardium* was noted.

From the locality on the left bank of the canal near Gatun practically the same fossils were collected as were found at Vamos Vamos with the addition of a *Cadulus*.

There can be no doubt that the rocks at Vamos Vamos, near Gatun, and at intermediate points as shown by borings, belong to the same formation, and they have been so regarded by Hill and Bertrand. The relation of these rocks, however, to the peculiar breccias and conglomerates at Bohio is not so clearly shown. Bertrand considers that the breccias at Bohio belong to the same series as those occurring in the central part of the isthmus which I have described as the Obispo formation, and he correlates them with the European Tongrian, that is, the base of the Oligocene in the Paris Basin section. This determination is based on fossils obtained from a boring at Kilometer 24·36. Here, according to Bertrand,* small nummulites of the Oligocene type are associated with *Orbitoides* that appear to be the same as those of the Peña Blanca marls (to be described later). The breccia, a part of the "Gamboa rock," is regarded, therefore, as certainly Oligocene and probably Aquitanian. In the geological profile accompanying Bertrand's report a special tint is given to the breccias, in order to accentuate the difference between these beds and the higher series, and they are referred tentatively to the Tongrian.

Hill appears to regard the breccia and perhaps the conglomerates at the French lock site as parts of an early igneous formation older than the Vamos Vamos beds. My own observations make me believe that the conglomerates at the lock site represent the lowest portion of the formation of which the Vamos Vamos beds and those in the vicinity of Gatun are the upper parts. This opinion is in accord with the local structure, the prevailing dip of the conglomerates, about 15 degrees to the northwest, being sufficient to carry them below the beds at Vamos Vamos. From a boring made by the Canal Commission at the Bohio lock site (Hole 24-b, K 24), fossils were obtained at elevations of from 20 to 40 feet below sea level that are believed by Doctor Dall to represent an Eocene horizon. They consist of fragments of *Lucina*, *Lima*, *Pecten*, *Cardium*,

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* Op. cit., p. 5.

Protocardia, and *Ostrea*, a small *Fusus* (?), a specimen of *Orbulina*, and a *Melanian* (?) associated with abundant fragmentary plant remains. The abundance of carbonaceous material and the presence of the fresh-water *Melanian* within a few feet vertically of the salt or brackish water species suggest delta deposits, and with this the physical character of the beds agrees perfectly, the fossils being preserved in calcareous sandstones or shales between beds of conglomerate precisely as are those exposed at the cutting for the lock site. Before reaching these fossiliferous layers the drill passed through a fine breccia like that shown at the quarries at Bohio, interbedded with which are fine-grained sandy layers containing plant remains. Conglomerates like those of the lock site were found below this breccia, then at about twelve feet below sea level a fine carbonaceous sandstone layer was encountered, and below this the fossiliferous sandstones.

On the strength of this evidence I am inclined to regard the conglomerates and breccias at Bohio as members, probably occurring near the base, of the formation that I have called the Bohio, and that they were laid down as delta deposits at the mouth of a large river, while the Vamos Vamos beds and those near Gatun were deposited contemporaneously in deeper water. It is entirely possible, of course, that the conglomerates may belong to an earlier epoch than the Claiborne, but the evidence for or against this is so meagre that in the absence of anything to the contrary it seems entirely reasonable to place the conglomerates at the base of the Clairbornian Bohio formation. No one can doubt the intimate relation between the conglomerates and the breccias nor that they are contemporaneous. It has been shown also that the conglomerate occurring in patches near Mamei and Gorgona rests unconformably upon the breccias of the Obispo formation. For this reason and as is also shown in the case of the Culebra beds, I believe that the Bohio rocks with their breccias are younger than the breccias of the Obispo formation instead of being a part of them as suggested by Bertrand.

Thickness of the Bohio Formation.—Of the thickness of the Bohio formation very little can be said. Borings on the "F" line at the Bohio dam site have brought up samples of the conglomerate, sandstone and breccia from nearly 200 feet below sea level, while at least 75 feet more may be added to this as exposed above sea level in the near-by hills. From Bohio to Gatun, where the Bohio formation is covered by younger beds, the distance is about seven miles in a straight line; assuming a uniform dip of only two degrees to the northwest, this would give at Gatun a thickness of nearly 1300 feet. At least 300 feet of the section has been shown in borings at Gatun.

Culebra Beds.

From near Empire to Pedro Miguel, a distance of about five miles along the line of the canal through the Culebra cut, are the best exposures of sedimentary rocks in the Canal Zone. The Obispo formation has been uncovered by excavation from Bas Obispo to a point about midway between Empire and Culebra, where it disappears beneath the sediments described by Hill and others as the Culebra beds. A considerable thickness of these beds has been exposed in the deepest part of the cut, beneath which borings have shown that they extend to at least 40 feet below sea level. A boring at Kilometer 55 passed through 207 feet of Culebra shales and sandstones without reaching the base of the formation. Nearly 175 feet should be added to this section as representing the part already removed from the canal prism at the point where the boring was made. This would give an observed thickness of nearly 400 feet. Hill estimated the thickness as at least 500 feet* and the total is probably greater rather than less.

So far as they have been exposed or explored by borings the rocks are found to be largely soft shales with abundant sandy, conglomeratic, and calcareous layers. At many horizons lenticular bodies of limestone occur. Although there are some thick beds of homogeneous pure clay shales, the majority of the rocks, whether sandstones, shales or conglomerates, are richly carbonaceous; lens-like seams of lignite have been found at many places in the cut and remains of trees and plants are abundant. The sandstones are impregnated with lime and in the coarser varieties of the rock films of the cementing calcite are readily visible. The conglomerates are composed of subangular rock fragments less than a quarter of an inch in diameter held in an impure calcareous matrix. The material of which all of the sedimentary Culebra beds are composed was derived from an older igneous land mass of which presumably the Obispo breccia was a part; quartz is notably absent and the colors range from bluish and greenish gray to nearly black in the richly carbonaceous beds.

In the upper part of the section at a number of places along the canal cut between Empire and Paraiso are extensive occurrences of andesitic breccias. Petrographically the fragments composing them closely resemble those of the Obispo breccia, but they are smaller and more uniform in size than those of the Obispo breccias of the same region. In the central area near Culebra summit these breccias are seen to rest upon the shales or fine sandstones of the Culebra beds. At the same locality there are numerous intrusive masses of basalt, and

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* Op. cit., p. 193.

faulting and considerable folding have taken place so that the relations of the various rocks are not perfectly clear. There can be no question, however, that the breccias are a part of the upper Culebra beds, for in several places a simple sedimentary contact between the two kinds of rock was observed, and it was even possible to collect hand specimens showing the transition from fine shales to the breccia. The breccias are at many places cemented by calcite of secondary origin. Specimens collected at Gold Hill (Cerro Culebra) and Paraiso, although considerably decomposed, may be recognized as made up of fragments of pyroxene-andesite of different textures, some of which have an abundant glassy groundmass. A boring near Paraiso (Kilometer 58) showed similar rocks at several horizons, while interstratified with them were other beds of sediments exactly like those in the lower or main part of the Culebra section. It would appear, therefore, that toward the close of Culebra sedimentation volcanic eruptions took place and that the ejectamenta were laid down conformably on the sediments; a number of such eruptions evidently occurred with intervals of quiescence, during which the deposition of the sediments continued. The association of these breccias with the Culebra sedimentary beds corresponds closely with that of the Bohio breccias and conglomerates with the exception that the Culebra breccias appear in the upper part of the section while those at Bohio seem to be near the base. Unfortunately the state of decomposition of the Bohio rocks prevents satisfactory petrographical comparison between the two breccias. In neither case does it seem possible to separate the breccias from the sediments as distinct igneous formations.

The relation of the Culebra sediments to the Obispo formation is more definitely shown than the Bohio rocks to the Obispo on the Caribbean side of the isthmus. At the surface the relations are not always clear, but it is possible by means of borings made at frequent intervals to trace the Obispo breccias from Bas Obispo south to a point near Empire, where they suddenly pitch in a southeast direction beneath the rapidly thickening cover of the Culebra beds. There is a moderate amount of local folding and faulting in the region and the Culebra beds have a prevailing dip to the southeast, but their inclination is much less than that of the southeasterly pitching surface of the Obispo on which they rest. Near Corozal the Obispo again appears at the surface, while between Corozal and La Boca borings have shown that there are present, beneath the alluvium, sandy shales precisely like many found in the Culebra section. As mentioned later in discussing the age of the Culebra beds, certain limestones that are thought to belong to the upper part of the shale series rest on the

Obispo breccias near Empire. The evidence between Culebra and Empire, at Corozal, and in the vicinity of La Boca seems to indicate that an unconformity exists at the top of the Obispo separating it from the Culebra beds. As has been shown, similar unconformable relations appear to exist between the Obispo and Bohio formations on the Atlantic slope.

Empire limestone.—Hill noted an occurrence of massive, semi crystalline limestone near Empire and from its relations in the field referred it to the Culebra beds.* I am not certain that I identified Hill's exact locality, but I did succeed in finding limestone of precisely the same character in the vicinity of the railway station at Empire on both the east and west sides of the track. Fifty feet east of the new station there are exposures, about ten feet thick, of a very massive cream-colored limestone in which I was unable to discover fossils; the outcrop is a small one and its relation to other rocks in the vicinity is not shown. About 150 yards west of this locality on the opposite side of the railway a greenish, impure sandy limestone, hard and compact, occurs beneath thin-bedded calcareous shales and sandstones, the whole exposure being less than ten feet thick. Fragments of a *Pecten* were found in this limestone but no determinable fossils. There are no exposures between these outcrops and the canal cut about one quarter of a mile to the northeast, at which point the Obispo formation is found close to where it disappears beneath the Culebra beds.

Elsewhere in the Culebra section lenticular bodies of limestone, less thick than the massive rock at Empire but otherwise of the same character, are found associated with the calcareous shales and sandstones, and it seems reasonable, as Hill has suggested, to regard the Empire occurrences as of this nature and belonging to the Culebra beds. The field relations, such as they are, appear to indicate that rocks of the Obispo igneous formation must lie within a few feet of the surface in the neighborhood of Empire, and it is not impossible that the limestone may rest directly upon them.

About midway between Empire and Las Cascadas on the Panama Railroad other limestones occur. They are less massive than those at Empire, in places gnarly and crumbling, and being practically at the surface where exposed in the railway cut are considerably weathered. Their color is buff or yellowish pink. The few fossils from this locality are poorly preserved and indeterminable, according to Dr. Dall, but he recognized a nullipore and two species of *Pecten* and suggests that this may be a reef deposit.

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* Op. cit., p. 195.

Nearer Las Cascadas bowlder-like concretionary masses of hard crystalline limestone, one to four feet in length, are preserved in red clays of decomposition near the railway and canal. Fragments of a *Pecten* and a tube-like *Xylotrya* were collected from one of these limestones but their age could not be determined.

Age of the Culebra beds.—Hill made a careful study of the Culebra beds, but only succeeded in finding fossils in the Empire limestone, mostly foraminifera that Bagg considered representative of the Eocene, and as quoted in Hill's report, he correlated this limestone with the Peña Blanca marl.* In material that I collected in the vicinity of Las Cascadas from rocks that I believed to belong to the same calcareous horizons as the Empire limestone, Dr. Dall failed to find any species from which the age of these beds could be determined. Bertrand and Zürcher, however, collected from the same localities and their material was determined by Douvillé as representing the Burdigalian Miocene, or the equivalent of the beds exposed at Kilometer 10 near Gatun.† The French geologists regarded the Empire limestone as belonging to the upper part of the Culebra beds and equivalent to the Vamos Vamos beds of the Caribbean slope. In the vicinity of Pedro Miguel Bertrand and Zürcher found fossils that were correlated with those from Las Cascadas. Fossils from my collection at the same locality were determined by Dr. Dall as probably representing an Oligocene reef deposit, while beneath them a typical Claiborne fauna was found in a compact impure limestone.

It is probable that the Claiborne horizon at Pedro Miguel is the one that Bertrand and Zürcher correlate with the beds at Las Cascadas, since the fauna of both is regarded by them as identical with that preserved at Kilometer 10 near Gatun. It is in collections from the Gatun locality made by Hill and myself that Dall finds his most typical Claiborne fossils. At both Pedro Miguel and Las Cascadas the position of the fossiliferous beds appears to be at or very near the top of the Culebra section, and in the absence of determinable fossils from lower horizons it seems reasonable to refer the Culebra beds as a whole to the same period as that in which the Bohio formation was deposited. The abundance of carbonaceous shales, seams of lignite and plant remains, together with fragments of a *melanian* found in the canal cut near Culebra, suggest that most of the beds below the limestone horizons were deposited in fresh water.

Limestones of the Upper Chagres.—Following the Chagres headward in a northeasterly direction from Matachin, where the river turns sharply to the northwest and flows toward the

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* Op. cit., p. 272, 275.

† Op. cit., pp. 6–9.

Caribbean, calcareous rocks similar to those near Las Cascadas and Empire are exposed at many places between Cruces and Dos Bocas, a distance in a straight line of about twelve miles. Between Cruces and Palo Grande compact limestone similar to that at Empire rests on carbonaceous shales like many in the Culebra beds. The rock is partly crystalline and contains in places fragments of shells. About one mile above the mouth of the Chilibre is the lower end of a winding gorge through which the Chagres flows for nearly twelve miles, the entrance to the gorge being a mile below Dos Bocas. The river, entrenching itself in an old valley, encountered between the points mentioned limestones and calcareous sandstones which offered greater resistance to erosion than the rocks to the northeast and southwest, so that its former meandering course has been preserved very perfectly, and at the outside curves of the meanders are nearly vertical cliff exposures of massive calcareous sandstone and limestone, in places more than one hundred and fifty feet high. Although the length of the gorge following the river is approximately twelve miles, the belt of hard rocks traversed is only about four miles wide.

The rocks are all of a light cream or buff color and range from partly crystalline limestones to coarsely granular rocks composed of broken shells, sands, specks of magnetite and occasional pebbles of igneous rocks held in a calcareous cement. Certain layers are well bedded, others massive, while cross-bedding is not uncommon. Fossils, *Ostrea* and *Pecten*, are abundant, but I was unable to find any determinable species; at a locality about a mile below Alhajuela a bed composed of broken corals and fragments of molluscan shells was found.

The similarity of some of these rocks and their fossils with those observed near Las Cascadas is striking, and Bertrand and Zürcher regarded the two occurrences as of the same age.* I agree with this opinion in so far as the Chagres and Las Cascadas beds are correlated with the fossiliferous rocks exposed by the canal at Kilometer 10 near Gatun, whose fauna, as has been said, Dall considers Claiborne Eocene; the French geologists have compared the Chagres rocks with beds near Marseilles that grade from Upper Oligocene to Miocene. Bertrand states, on the authority of M. Boutan,† that the limestone near Dos Bocas resembles in part certain marls occurring at Peña Blanca, and that it contains foraminifera. I am not prepared to say that this is not the case, but the structure of these beds as noted both by Bertrand and myself would carry them beneath the limestones of the gorge, and they should correspond closely in position to the limestones observed near Cruces and therefore be comparable to the Empire limestone.

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* Op. cit., p. 10.

† Op. cit., p. 10.

MARLS OF PEÑA BLANCA.

(*Lower Oligocene.*)

Less than a quarter of a mile west of the railway station and quarries at Bohio at the base of a low hill are outcrops of a hard, light yellowish marl. A quarter of a mile still farther west the same rock has been exposed in excavations for a diversion channel made by the French. The rock as a whole may be described as a thick-bedded marl, buff to cream-colored, and containing foraminifera in greater or less abundance, the most typical being *Orbitoides fortisi.* Sparsely disseminated through the rock are minute specks of a dark silicate and fragments of feldspar. So far as is known, the only occurrences of this rock are at the localities mentioned between Bohio and Peña Blanca.

Nowhere in the vicinity of Bohio was I able to discover the relation of the Peña Blanca rock to the Bohio conglomerate or breccia, nor is any direct evidence found in the borings, but from the general field relations it would seem that the marls are younger than the breccias, since less than half a mile east of the marls borings have indicated the presence of the breccias and conglomerates many feet below the observed elevation of the marls, while as shown at the lock site exposures, the Bohio rocks dip about fifteen degrees in the the direction of the marls. Unless a fault of considerable magnitude occurs between the two localities, of which there is no evidence, the marls cannot be older than the Bohio beds, nor is there any indication that they were contemporaneous deposits, borings between Peña Blanca and Vamos Vamos having passed through rocks of the Vamos Vamos facies of the Bohio alone. Hill states* that he found the foraminiferal marls in uncomformable contact with the conglomerates at a locality known as Peña Negra, one mile below Bohio. I was unable to identify this point, but Hill's observation is in entire accord with my opinion that the foraminiferal beds of Peña Blanca rest uncomformably on the rocks of the Bohio formation.

Hill regarded the Peña Blanca beds as older than the Vamos Vamos, basing his opinion on the northwest dip of the Vamos Vamos beds and the position of the foraminiferal marls southeast of them. I have shown, however, that in all probability the Vamos Vamos beds and the Bohio conglomerates belong to the same formation, and the discordance between the Peña Blanca and Vamos Vamos beds is to be considered as another manifestation of the same unconformity observed by Hill at Peña Negra. This view agrees with Dr. Dall's opinion that the Peña Blanca marls, on account of the presence of the charac-

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* Op. cit., pp. 178–179.

teristic species *Orbitoides fortisi*, are of Lower Oligocene age corresponding to the Vicksburg.

MONKEY HILL FORMATION.

(*Upper Oligocene.*)

Between Gatun and the coast at Colon is a more or less hilly region in which numerous exposures may be found along the lines of the Panama Railroad and the French canal. Fossils collected from the rocks at these points indicate that all of the beds are of the same age. The rocks are well stratified, often thin bedded, calcareous sandstones, argillaceous sandstones, marls and shales, usually fine grained and even-textured, and when fresh of a neutral bluish or greenish gray color. They belong to what Hill called the Monkey Hill beds,* the best exposures at the time of his visit being near the Panama Railroad where it passes through the hills. At the time of my examination by far the best exposures were at Gatun, where extensive excavation had been made for the locks. At this point also it is believed that the base of the formation is shown. In order to avoid ambiguity these beds will be referred to as the Monkey Hill formation, as they were so described by Hill, although in my report to the Canal Commission they were spoken of as the Gatun beds, since they made up a large part of the rocks through which the locks at Gatun were to be constructed.

From fossils collected both by Hill and myself at Monkey Hill and Gatun, Dr. Dall considers that the Monkey Hill formation is equivalent to the Chipola Oligocene, that is, younger than the Vicksburg or the *Orbitoides* marls of Peña Blanca. Among the species recognized are:

Cardium sp.
Liocardium serratum Linn.
Psammobia
Cytherea
Abra
Tellina
Chione

Turritella
Oliva sp.
Cadulus
Cerithiopsis
Agriopoma
Cyclinella.

Directly below and within a foot or two of the point where these fossils were collected at Gatun is a coarse conglomerate also containing numerous fossils that are pronounced by Dall as of the same age as those found near Gatun in the Bohio beds. The conglomerate appears to grade upward into the fine calcareous sandstone or marl that contains the younger fossils, and were it not for the definite indication of greater

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* Op. cit., 176–177, 208.

age from the fossil evidence, I should be inclined to consider this conglomerate a basal member of the Monkey Hill formation; it is, of course, not impossible that this may be the case and that the fossils were derived from the erosion of the older Bohio terrane. Less than half a mile in a straight line from this locality is the point where the Bohio (Claibornian) fossils were collected at the edge of the French canal near Gatun (Kilometer 10), and the general dip of the beds at this locality is in the direction of the conglomerates exposed at Gatun. In any event the base of the Monkey Hill formation must be very near the conglomerate, whether actually at the top or including the conglomerate. Unfortunately there are no other exposures in the vicinity to throw light on this matter and little can be learned from the drill records. The conglomerate is clearly shown by a number of borings, below which are beds of a white pumiceous tuff associated with other conglomerates similar to the uppermost one, and calcareous sandstones and marls. Beneath these beds are fine calcareous or argillaceous sandstones of uniform composition that undoubtedly belong to the Bohio formation.

At Gatun about eighty feet of the Monkey Hill formation is shown, but, as in the case of the other sediments, it is only possible to give an approximate estimate of the thickness of the whole formation. From rough calculations, assuming low dips of from one to five degrees from Gatun northward, there should be a thickness of at least five hundred feet in the vicinity of the Monkey Hills near Colon, while perhaps from two to three times this thickness may exist. To the west, where the Chagres leaves its main valley and passes through a younger valley to the sea, a thickness of from one hundred and fifty to two hundred feet is actually shown in the hills, while as much more must exist beneath the present floodplain of the river if the dips observed in the region are at all regular.

No rocks corresponding in age to those of the Monkey Hill formation have been observed on the Pacific side of the isthmus.

The lithologic character of these rocks is essentially the same as that of the finer-grained Bohio rocks. They are composed almost entirely of the debris of igneous rocks, in some cases the particles being exceedingly fresh, but commonly decomposition and fineness of texture make it impossible to say whether the material was derived directly from volcanic eruption or from the degradation of an older land surface. I am in favor of the latter hypothesis, inasmuch as no evidence has been found elsewhere of contemporaneous eruptions.

IGNEOUS ROCKS.

Acid Porphyries and Tuffs.

The oldest igneous rocks, the breccias of the Obispo formation, have already been described, and it has been shown that eruptions of much the same character continued intermittently for some time during the period of early Tertiary sedimentation. After an interval of quiet, eruptions of an entirely different sort of rock took place either at the close of the Bohio epoch or at the beginning of the Monkey Hill. These later eruptives are largely fragmental and are found on both the Atlantic and Pacific sides of the isthmus. The massive rocks of this period are best shown at Ancon Hill, which is composed entirely of rhyolite porphyry. Almost completely surrounding Ancon Hill, the continuity being broken only on the west by a later intrusion of pyroxene-andesite, are tuffs and fine breccias of the same composition as the rhyolite porphyry of the hill. The tuffs are well bedded and in some places quite massive, individual beds varying from six inches to five or six feet in thickness; they are fine-grained and, where exposed near the surface, usually altered to a white clay.

Beds similar to those in the vicinity of Panama are exposed between San Pablo and Tabernilla on the Atlantic slope, the best outcrops being along the Chagres River near the point where the Panama Railroad crosses northwest of San Pablo.

These comparatively siliceous rocks are the ones that Hill placed in his Panama formation; he referred to them as rhyolitic tuffs,* while Bertrand considered them as trachytic.† Specimens that I collected from various points showed greater or less decomposition in most cases and none was sufficiently fresh for chemical analysis. A microscopical study shows that they are all closely related and that in addition to the occurrences mentioned, certain intrusives in the Culebra beds probably belong to the same series. It is impossible to group all these rocks under one descriptive head such as rhyolite tuff or trachyte tuff; certain facies are distinctly rhyolitic, others trachytic, while forms near quartz-bearing latite are not uncommon.

The rock of which Ancon Hill is composed is a creamy-white porphyry with phenocrysts of feldspar in a fine felsitic groundmass; occasional specks of an altered dark mineral are present. Microscopically the rock is seen to be a porphyry with phenocrysts (mentioned in order of relative abundance) of albite, quartz, and orthoclase in a groundmass containing abundant orthoclase, some quartz and a little albite. Slight kaolinization of the feldspars has taken place, and the ferro-

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* Hill, op. cit., 199–202.

† Bertrand, op. cit., 9, 23.

magnesian mineral, altered beyond recognition, has stained the rock slightly with iron oxide; there is no indication that the dark silicate was an important constituent. Another specimen of the same rock from a near-by locality showed little or no porphyritic texture.; a few fragments of orthoclase and laths of oligoclase are present, with many large irregular patches of quartz; there is some magnetite and limonite but apparently no ferro-magnesian mineral.

The islands of Naos and Culebra in Panama Bay, between three and four miles from Ancon Hill, are composed of a similar porphyry containing a moderate number of phenocrysts of plagioclase ranging from andesine to a labradorite (Ab_2An_3), and hornblende. The groundmass is holocrystalline and consists of orthoclase and plagioclase in about equal amount with traces of hornblende, usually altered to chlorite, some magnetite, and quartz.

Closely related to the rock of Naos Island is an intrusive sill found in the beds at Culebra north of Gold Hill (Cerro Culebra). This rock is a fine-grained porphyry with a fluidal base, largely glassy, but containing a few microlites of plagioclase and minute grains of orthoclase. The phenocrysts are mostly andesine although labradorite is present. A dark mineral, perhaps hornblende, was observed in several specimens, but in all cases it has been considerably altered. In one specimen it was impossible to decide whether the altered mineral had been hornblende or biotite, the ragged form suggesting the latter. Near Las Cascadas, and associated with the Obispo breccia, a dense rock with a marked fluidal texture is exposed at several places. Under the microscope it is found to consist of a partly glassy groundmass, laths of plagioclase, a little orthoclase and an abundance of fine grains of magnetite. The few plagioclase phenocrysts are considerably decomposed and ferro-magnesian minerals are notably absent.

All of these rocks, with the exception of the Ancon porphyry, appear to be intermediate between true rhyolites and latites, with perhaps a stronger tendency toward the latitic form; the impossibility, however, of determining the exact character of the groundmass in most cases prevents a definite classification by microscopical methods, and none of the specimens, as has been said, was sufficiently fresh to warrant chemical analysis. The tuff exposed by the Chagres River in the vicinity of San Pablo consists of small fragments of fibrous or vesicular glass or pumice of low specific gravity; there are occasional particles of plagioclase and orthoclase crystals but no quartz. A greater textural variation is found in the tuffs in the vicinity of Panama; they are less pumiceous and consist of fragments of rock essentially the same as that of Ancon Hill.

The relation of the tuffs and fine breccias in the vicinity of Panama to Ancon Hill suggests that the pyroclastics were derived from a volcanic center now marked by the massive porphyry of Ancon. The tuffs, as has been said, are well stratified and surround Ancon Hill except in the vicinity of Sosa; they dip away from Ancon Hill at all points and in a few instances have been found to be cut by dikes that appear to radiate from the hill as a center. No local source or center of eruption for the tuffs on the Atlantic slope has been found, and it is possible that they may have been derived from the Ancon eruptions, the distance between the points being only twenty miles. The extremely light pumiceous character of the San Pablo deposits would favor this view.

The age of the acid eruptives is fairly well shown at several places. Near Panama evidence from borings quoted by Bertrand* indicates that the acid tuffs are younger than the Culebra beds and rest upon them. I was unable to find boring records at the localities mentioned by Bertrand, but the field relations fully justify Bertrand's view. The Culebra beds disappear beneath the surface of the lower Rio Grande Valley near Pedro Miguel, and at Miraflores the acid tuffs are well exposed at a number of points. Borings made in exploring for dam sites between Sosa Hill and Corazal and also across the mouth of the Rio Grande indicate the presence of sediments similar to those of the Culebra beds at approximately seventy or eighty feet below sea level, and one boring near La Boca showed a dike of rock similar to that of Ancon Hill cutting these sediments. On the Atlantic side between San Pablo and Tabernilla there is no surface evidence bearing on the age of the acid tuffs. Borings for a dam site near San Pablo indicate rocks similar to those of the Bohio breccias, beneath what I believe to be tuffs of the acid series, but the advanced decomposition of the rocks makes it difficult to distinguish one from another, and the supposed tuffs may be sandstones of the Bohio formation. It was mentioned, in describing the Gatun occurrence of the Monkey Hill beds, that beneath the uppermost conglomerate borings revealed the presence of one or more beds of extremely fine white pumiceous tuff, and recent excavation for a road from the old Gatun railway station to the encampment at the top of the hill has exposed the tuffs. They are clearly interstratified with the sediments, but as previously stated, it is difficult to determine the base of the Monkey Hill beds, so that the tuffs may be regarded as lying either at the top of the Bohio or at the base of the Monkey Hill formation. In either case there can be no doubt that they are younger than the Eocene sediments and not Cretaceous, as supposed by Hill.

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* Op. cit., 8-9.

Basic Intrusives.

The last phase of eruptive activity of which there is evidence in the Canal Zone is represented by numerous basic intrusives that occur in great abundance in the central and southern parts of the isthmus. To the north, on the Atlantic coast, they are exposed in the vicinity of Porto Bello, and about eighteen miles east of Colon. Between Gorgona and Pedro Miguel most of the hills are composed of the basic rocks. In all observed occurrences the rocks are intrusive in the older formations and most commonly occur as large stock-like masses; dikes are numerous but no surface flows have been found. The rocks that have been collectively referred to as basic intrusives are pyroxene-andesites or basalts. All are notable for the calcic character of the feldspar, which is frequently bytownite or anorthite. Augite and magnetite are abundant and many of the rocks contain considerable orthorhombic pyroxene. The majority of the rocks are pyroxene-andesites, but basalts are common and in one or two instances were found to contain much olivine; practically all have more or less glass in the groundmass and some are vesicular. Although undoubtedly related to the andesites from which the Obispo breccias were derived, none of the Obispo rocks shows the extremely basic character of many of the later intrusives.

At many places in the interior the basic intrusives may be seen cutting the older sedimentary rocks, while the relations near Panama seem to indicate that the andesite of Sosa Hill has been intruded into the rhyolitic tuffs of Ancon. So far no basic rocks have been observed to cut the Monkey Hill formation, but the large masses of pyroxene-andesite at Porto Bello are probably intrusive in these sediments although no contacts have been observed. The very uniform lithologic character of the Monkey Hill beds, and the lack of any observed unconformity indicating decided crustal movements such as must have accompanied the intrusion of the andesites, would seem to show, in the absence of any more direct evidence, that the period of basic intrusions followed the Monkey Hill epoch and may have been the immediate cause of the termination of that long period of quiet sedimentation.

Distribution of the Rocks.

Unfortunately little is known of the areal distribution of the various formations that have been described. The section exposed along the canal line is fairly complete and in places it has been possible to trace certain of the formations a few miles beyond the boundaries of the Canal Zone, but even if greater areas had been examined it is doubtful if any more definite information in regard to the limits of the different formations could have been obtained. To a moderate degree the character of the topography may be taken as a guide and the known distribution of the different sorts of rocks thus slightly extended. This applies more especially to areas of sedimentary rocks as contrasted with those of igneous formations.

Obispo breccias.—In the vicinity of Matachiń Obispo breccias form the hills north of the Chagres, but the surface extension of the formation in this direction can not be great, for, not more than four miles northwest of Matachin, younger sediments are exposed in the neighborhood of Tabernilla and Frijoles. From Matachin southeasterly the breccias occur on both sides of the canal, in places covered by the Culebra beds, beneath which they eventually disappear between Empire and Culebra; they again make their appearance in the vicinity of Corozal and they have been noted at several places in the hills traversed by the old Cruces trail northeast of Miraflores and Pedro Miguel. The breccias are particularly well shown in the rolling country northeast of the city of Panama near Las Sabanas. From borings, the Obispo is known to occur as far north as San Pablo, but beyond that point there is no evidence of its existence.

Basic intrusives.—Although the basic intrusives are not limited to any particular part of the isthmus, they are most abundant in the areas characterized by the Obispo breccias. In the Culebra region they are especially numerous, and are believed to make up a large part of the mountainous region southwest of the city of Panama along the Pacific coast; near the shore are many exposures of columnar basalt that have been observed beyond the mouth of the Chorrera River, 18 miles southwest of La Boca. No basic intrusives have been found northwest of San Pablo in the Canal Zone, but at Porto Bello, about 18 miles northeast of Colon, pyroxene-andesites are exposed at the water's edge and occur in many of the near-by hills.

Acid eruptives.—The rhyolitic rocks and others related to them occur in two general areas. One of these is at Panama, where the well-bedded tuffs surround the central mass of rhyolite porphyry of Ancon Hill. The fragmental rocks underlie the city and extend as far north as Miraflores. Similar rocks are also found on the southwest side of the Rio Grande opposite La Boca, while massive rock like that of Ancon Hill composes the islands of Naos and Culebra in Panama Bay. Hershey has reported similar rocks more than one hundred miles to the southwest near Santiago.* The

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* The Geology of the Central Portion of the Isthmus of Panama, Oscar H. Hershey, Bull. Dept. of Geol., Univ. of Cal., vol. ii, p. 244, 1901.

second area, in the vicinity of San Pablo and Tabernilla, is probably more restricted than that of the Pacific side. The rocks are best exposed along the Chagres River near San Pablo, but the hills extending northward from Barbacoas, where the Panama Railroad crosses the Chagres, are composed entirely of these acid pyroclastics. Their exact northwestern limit is unknown but probably lies at some point between Buena Vista and Tabernilla. Similar rocks are found in the vicinity of Gatun interbedded with the sediments at that locality.

Sedimentary rocks.—A little more is known in regard to the distribution of the sedimentary formations. So far as my observations go, the Culebra beds are restricted to the occurrences in the Culebra district with a probable extension as far south as La Boca suggested by borings. On the northern side the sediments from the Bohio formation up to the Monkey Hill have a much wider distribution. The sediments extend from Limon Bay along the line of the canal to Bohio at least, and remnants of the Bohio formation have been found as far south as Matachin. The subdued topography characteristic of areas of these young sedimentary rocks extends in a northeasterly direction from Colon almost to Porto Bello and throughout this distance I believe that sedimentary rocks are the only ones represented at the surface. Between this coast belt and the interior, where the limestones of the upper Chagres are exposed, is a region of some elevation concerning which there is no information whatever except quite near the canal line, at Tabernilla and Frijoles, where poorly exposed sediments containing lignite are known to occur. Southwest of the canal line and along the Atlantic slope sediments have been traced for nearly twenty miles up the valley of the Trinidad River. The rocks of this region are of the same character as the Bohio or Monkey Hill formations; they are exposed at a few places along the water's edge, but the rock at these outcrops is in an extremely decomposed condition and no fossils were discovered. On the Pacific coast southwest of the city of Panama and beyond the range of hills composed of basic intrusives is the broad low valley of the Chorrera, that, on account of its very subdued topography, looks as if it had been eroded in sedimentary rocks. The Chorrera River rises near the head waters of the Trinidad and it is not improbable that the sedimentary rocks extend across the divide and down the Chorrera to the Pacific. According to Lull,* coal, probably a lignite, occurs in the drainage of the Rio Indio,

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* Reports of Explorations and Surveys for the location of Interoceanic Ship Canals through the Isthmus of Panama, E. P. Lull, U. S. N., Washington, 1879. Pp. 30–32.

and the deposits may be reached from the Pacific side by ascending the Chorrera River. The locality is indefinite, but cannot be far from the head waters of the Trinidad, where similar lignites have been reported.

Structure.

The broader features of the geological structure of the isthmus are simple. In the Canal Zone the sedimentary rocks of the Atlantic side dip toward the coast at moderate angles while on the southern side of the isthmus the inclination of the Culebra beds is in the direction of the Pacific. It has not been possible to discover any marked characteristic structure in the Obispo breccias; in the central region the few contemporaneous flows appear to be nearly horizontal, while no evidence of stratification can be made out in the occurrences near Panama and Las Sabanas.

When examined in greater detail it is found that the inclination of the older sediments on the Atlantic side of the isthmus is greater than that of the Monkey Hill beds. The strikes also are different; that of the Bohio formation, best shown at Bohio and Vamos Vamos, being about northeast-southwest, while the Monkey Hill beds at Gatun strike more nearly east and west. This agrees with the evidence of unconformity between the Bohio formation and the *Orbitoides* beds of Peña Blanca. No indication of marked faulting has been discovered in the region north of Empire, although local fracturing and minor dislocation have occurred at places where the folding appears to have been pronounced as at Vamos Vamos, according to Hill, and to a minor degree at Gatun.

The acid tuffs at San Pablo are inclined to the northwest at angles of from five to ten degrees; with the exception of isolated patches of Bohio conglomerate near Matachin these are the last beds encountered, following the canal southward, in which any structure can be made out until the Culebra beds are reached near Empire.

South of Empire greater structural complexity exists. The Culebra beds are locally folded, but have a general southeasterly dip of from ten to fifteen degrees. At several points the Culebra cut is crossed by small faults, the downthrows of from ten to fifty feet being to the southeast. At the deepest part of the cut, where the canal passes between Gold Hill and Contractor's Hill, the Culebra shales with the breccias in the upper part of the section have been intruded by basalt and since intrusion have suffered faulting. The mass of Gold Hill has dropped as a block or wedge between the beds on either side, being bounded on the north and south by faults; during the process of faulting, the sediments, previously deformed by the intrusions of basalt, were still further twisted and now dip at angles of sixty degrees or more to the northeast into Gold Hill.

Between Culebra and the Pacific the structure is simple. The Culebra beds, frequently intruded by broad dikes of basalt, are gradually carried by their prevailing southeast dip beneath the level of the Rio Grande valley not far from Pedro Miguel. From Miraflores to the outskirts of the city of Panama the acid tuffs have been locally folded, but in the neighborhood of Ancon Hill and under the town their structure, as already mentioned, appears to be due to initial dips of the beds deposited on the flanks of the old Ancon volcano. That is, in tracing the beds from north of Ancon around the hill to a point on the shore close to Sosa Hill the strike is found to swing through an angle of nearly one hundred and eighty degrees; the dips range from five to fifteen degrees, the steeper inclination being found near the base of Ancon Hill.

Reviewing these facts, the structure of the isthmus appears to be characterized by a dominant arch or broad anticline with its axial trend between east-west and northeast-southwest, the crest of the arch being in the south-central part of the isthmus near Bas Obispo. The northern limb of the anticline is of moderate inclination, while the southern limb, near the crest of the arch at least, is steeper. The limestones and calcareous sandstones of the upper Chagres are nearly at the crest of the fold and their prevailing southwest to west dip suggests that the anticline pitches to the southwest. Whether this is a broad structure or comparatively local is not known, no evidence having been found in the country southwest of the Canal Zone. It is probable that the westward pitch is more than a mere local cross fold and due to the same uplift that formed the San Blas Range to the east. Unfortunately there is little or no trustworthy information as to the geology of these mountains other than that they are believed to have a core of granular rock* intruded in late Tertiary time. It must be borne in mind, however, that there is evidence of a decided orogenic movement in this region in late Eocene time that caused the unconformity at the base of the Peña Blanca *Orbitoides* beds; it is not impossible that the supposed southwest pitch of the anticline may be due to the earlier deformation.

Washington, D. C.

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* Hill, op. cit., pp. 211–213.

SCIENTIFIC INTELLIGENCE.

I. GEOLOGY.

1. *Geology of the Adirondack Magnetic Iron Ores;* by D. H. NEWLAND, with a *Report on the Mineville–Port Henry Group;* by J. F. KEMP. N. Y. State Mus. Bull. 119, 8°, pp. 182, pls. and maps. Albany, 1908.—This work gives a detailed description of the geology, petrography, and occurrence of the iron-ore bodies in the eastern and northern Adirondack region. It contains also much material relating to the history of the minerals and mining of the area. It will no doubt prove of great service to those locally concerned in these deposits, and contains much of interest to those engaged in economic geology and in the study of ore deposits. From the descriptions given it would appear that the unusable titaniferous ores are magmatic segregations of the gabbro-anorthosite masses (p. 149); while the purer and worked magnetites, which have a different method of occurrence, are probably, in part at least, due to pneumatolytic processes as suggested by the presence of fluorite in the Palmer hill and other mines (pp. 31–33 and 100). L. V. P.

5. *Geologische Prinzipienfragen;* von E. REYER. Pp. 202, 254 figs. Leipzig, 1907 (Wm. Engelmann).—There was a time, in the recollection of older geologists, when Reyer's name was associated with the active publication of works on various geological subjects and on the geology of particular regions, marked by a highly theoretical and, at times, imaginative treatment. In the present work the author states that finding his views, especially those relating to the origin of mountain ranges, not generally accepted, he engaged in lines of work other than scientific, but now, convinced that eventually his experiments and views must prove of service, he feels it incumbent upon him to publish them in a general statement. While it would be entirely out of place in this brief notice to enter into a critical discussion of the author's views on fundamental geological problems, it may be mentioned that some of the more important subjects treated relate to the origin and manner of igneous intrusions and extrusions, to the part played by volcanic islands, to the igneous phenomena as displayed in the Alps, to the origin of mountain ranges, to elevation and depression of the crust, etc. The author says frankly at the outset that he expects opposition to his views, which, in many cases at least, depart widely from those generally held to-day, and in some instances represent theories which have been discarded in the evolution of geological science. While this is true, the work is at least suggestive, and even if the reader does not accept the presentation of the particular theses discussed, he may find a strong sidelight cast on some special problem in which he is interested. L. V. P.

2. *Die Entstehung der Kontinente, der Vulkane und Gebirge;* von P. O. KÖHLER. 8°, 58 pp., Leipzig, 1908 (Wm. Engelmann).—

These are momentous questions to be considered and answered in 58 pages, and therefore the author does not waste time in preliminaries, or in consideration of details. He believes that the view, often advanced, that the features of the earth mentioned in the title are caused by the contraction of a cold crust settling down to fit a still hot, but cooling and contracting, nucleus, is essentially wrong. He essays to prove that the crust is losing heat faster than the interior, and that this interior, as compared with the outer shell, is relatively stable. The latter, instead of being under contractional stresses, is in a state of tension. The relative movements of the outer surface, which give rise to earth features, are ascribed to the action of water, which penetrating downward to the heated zone below, returns in a hot condition, warming the superincumbent masses and thus causing them to expand. By this mechanism, in various ways, he endeavors to show that the continents, volcanoes, and mountain ranges are formed.

While it is not probable that this brochure will be taken very seriously by those who still hold by the nebular hypothesis of the earth's origin, and will seem to followers of Chamberlin's planetesimal hypothesis much like a charge upon windmills, it may be still said that it is well and clearly written, and in places contains suggestive ideas. L. V. P.

3. *Geological Survey of Canada;* A. P. Low, Director.—The following publications have been recently issued :

Annual Report, New Series, Volume XVI, for 1904 ; this contains Reports A, B, C, CC, G, H and S and is accompanied by a series of fourteen maps. Ottawa, 1906. It is stated that this volume is the last to be published in this form, the plan being to present in future each report as a separate publication.

Summary Report for the calendar year 1906 ; pp. 206. Ottawa, 1906.

The Falls of Niagara ; by J. W.W. SPENCER, 1905–6. Pp. xxv, 490, with 43 plates and 30 figures. Ottawa, 1907. This volume was noticed in an earlier number (vol. xxv, p. 455).

Report on Gold Values in the Klondike high level Gravels ; by R. G. MCCONNELL. Pp. 34, with one plate and a geological map.

The Telkwa River and Vicinity, B. C. ; by W. W. LEACH. Pp. 27, with a geological map. Ottawa, 1908.

Report on a portion of Northwestern Ontario, traversed by the National Transcontinental Railway, between Lake Nipigon and Sturgeon Lake ; by W. H. COLLINS. Pp. 23, with a geological map. Ottawa, 1908.

4. *Geography and Geology of a Portion of Southwestern Wyoming,* with special Reference to Coal and Oil ; by A. C. VEATCH. Prof. Papers, 56, U. S. Geol. Surv., pp. 178, 1907 (=1908).—This is a very important paper for statigraphers and paleontologists, and, especially, for those interested in the discussion as to whether the Upper Laramie is to be referred to the Mesozoic or the Tertiary. The author shows that the Cretaceous

of this region "has the enormous thickness of over 20,000 feet," and is a conformable series, beginning with the Bear River formation, and closing with the Adaville formation=Lower Laramie. Then followed "a long period of folding, faulting and erosion." Angularly unconformable with the Cretaceous series are the Evanston, Almy and Fowkes formations, followed by another period of "folding and erosion of great magnitude though of much less importance" than the earlier one. The Almy and Fowkes formations "have without exception been considered Eocene," and, as they are conformable with the Evanston, all are regarded by Veatch as best placed in the Eocene. "The uncomformity at the base of this series [Evanston, Almy, and Fowkes] amounts to over 20,000 feet; that at the top amounts to perhaps 5,000 feet, but this is of much less relative significance than the figures indicate, because the movements of the second disturbance were along lines of weakness produced by the first. The physical break between this group and the known Cretaceous beds is thus greater than the break between it and the known Eocene, and, on purely physical grounds, this group would seem to belong rather to the Eocene than to the Cretaceous" (p. 75–76). C. S.

5. *Einführung in die Paläontologie;* von GUSTAV STEINMANN. Second edition, pp. 542, with 902 text-figures. Leipzig, 1907 (Wilhelm Engelmann).—This well-known introduction to paleontology has been enlarged and brought up to date. It treats of plants (pp. 13–74), invertebrates (75–388), and vertebrates (389–514). All of the more important groups of forms found fossil are defined and illustrated, so that any beginner in paleontology may obtain a good knowledge of the hard parts of extinct organisms. No detailed classifications appear, nor is there any extended discussion of lines of descent. The book presents what is known of the leading forms in each group of organisms in short synoptic form. The illustrations are wood-cuts and line drawings, made especially for this book, and are abundant and adequate. C. S.

6. *Niagara Stromatoporoids;* by W. A. PARKS. Univ. Toronto Studies, Geol. Ser., 1908, pp. 175–240, pls. 7–14.—Professor Parks here continues his detailed studies on American Silurian stromatoporoids. At least 34 forms are described, many being new. Chalazodes is the only new genus. C. S.

7. *On an Occurrence of Hybocystis in Ontario;* by W. A. PARKS. Ottawa Nat., XXI, 1908, pp. 232–236, pl. 2.—Very excellent material of this obscure echinoderm has been found near Elton, Ontario. The material is described and figured in detail, indicating, the reviewer thinks, cystid rather than blastid characters. C. S.

II. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *Publications of the Japanese Earthquake Investigation Committee.*—Nos. 22 A and 22 C of this issue have recently been received, also Vol. II, No. 1, of the Bulletin of the Committee. This last contains 8 articles by Prof. F. Omori, all of inter-

est to those concerned with seismology. One of these is an interesting discussion on microtremors and another gives a list of prominent Japanese earthquakes between 1902 and 1907.

In No. 22 C an account is given by T. Wakimizu of a new volcanic island in the Iwôjima group, remarkable because of its ephemeral character. On February 1, 1905, this island was 3 miles in circumference and 480 feet in height, but on the 16th of June it was reduced to a low reef only 1,500 feet long and less than 10 feet high. In June of the present year it is stated that the new island was entirely buried by the sea. Interesting accounts are also given of the other islands of the group, accompanied by a series of excellent plates.

Volume xxiv of the Journal of the College of Science, Imperial University of Tokyo, is devoted to an investigation of the secondary undulations of ocean tides, carried out by the order of the Earthquake Investigation Committee during 1903–1906. It is accompanied by 95 plates, maps and charts. The authors are K. Honda, T. Terada, Y. Yoshida and D. Isitani.

2. *The Physical Basis of Civilization;* by T. W. HEINEMAN. Pp. 241. Chicago, 1908 (Forbes & Co.).—The author advances the theory in this book that the physical, mental, moral, and social conditions of the human race are due to two comparatively slight structural modifications of the ape-like ancestors of man: first, the lengthening of the foot by the modification of the great toe, which gave man a position on his feet of far greater firmness than that of any existing apes; and second, the position of the skull with reference to the spinal column, on account of which the erect position of the body is more readily maintained. As a result of the specialization of the feet for supporting the body firmly, the hands were left free for grasping and handling and the sense of touch became more highly developed so that a more efficient means of acquiring knowledge of surrounding objects was opened to man; likewise, the elevation of the special sense organs high above the ground by the erect attitude widened the range of their usefulness and thus led to the increase of the intelligence of man. The upright position, and consequent exposure of the vital organs to attack, and the comparative defenselessness of the human species, rendered his survival in the struggle for existence dependent upon conduct to a greater extent than in any other known animals, and the extreme disability of the pregnant female made the devotion of the male to his mate and the establishment of the family relationship necessary conditions for the survival of the race. B. W. K.

3. *General Physics. An elementary Text-book for Colleges;* by HENRY CREW. Pp. xi, 522 with 40 figures. New York, 1908 (The Macmillan Co.).—This text-book is in its treatment distinctly above the plane of the high school type, and yet, without sacrifice of accuracy, maintains throughout a simple, lucid exposition of the fundamental principles of the subject. The scope of the book is obvious from the title and number of pages stated above. The presentation of the subject matter is excellent. There is in it little to suggest the older purely descriptive

texts and happily less of the more recent tendency toward a presentation so severe as to engender in most beginners a hatred, rather than a love of the subject. The author has adopted, in general, if not uniformly, a happy method of leading up to principles through a simple discussion of the knowledge already in the student's possession. The mathematical expressions are developed in a natural and consistent manner and are made to serve effectively both in summarizing the respective topics and in revealing to the student "the essential unity of the subject." Practically all of the illustrations are diagrammatic and clear. Problems are found in ample number and variety. The text lends itself readily to abridgement or amplification, and taken as a whole this appears to be one of the best recent text-books.

D. A. K.

4. *Die Insektenfamilie der Phasmiden;* bearbeitet von K. Brunner v. Wattenwyl und Jos. Redtenbacher. II Lieferung, pp. 181–340; III Schluss-Lieferung, pp 341–589, with plates xvi–xxvii. Leipzig, 1908 (Wm. Engelmann).—The first part of this monumental work on the Phasmids appeared in the spring of 1907 (see vol. xxiii, 398). The two parts now issued complete the work. Of these the second is devoted to the Clitumnini, Lonchodini and Bacunculini; it has been prepared by the senior editor. The third and concluding part embraces the Phibalosomini, Acrophyllini, and Necrosciini and has been worked up by Prof. Redtenbacher. The whole work is admirably thorough and is based, not only upon the very extensive private collections of the authors, but they have also taken advantage of the material in various public museums, especially those in Europe, which have most freely placed their collections at their disposal. The publication of the whole work in the liberal form presented, with its numerous plates, has been made possible through the support of the Imperial Academy at Vienna, the funds being furnished by the Treitl Foundation.

5. *Les Dépôts Marins;* Léon W. Collet. Pp. 325, with 35 figures. Paris, 1908 (O. Doin).—This volume forms one of the issues of the "Encyclopédie scientifique" which is being published under the direction of Dr. Toulouse. If carried through on the very liberal scale planned, the Encyclopedia will include 40 sections, aggregating about 1000 volumes.

The work in hand is one of seven volumes, to be devoted to physical oceanography, which are in charge of Dr. J. Richard. The author, who has studied with Sir John Murray at Edinburgh, presents here an excellent summary of the whole subject of marine depositions, giving the results contained in the well-known work by Murray and Renard on Deep Sea Deposits, and also bringing the various branches of the subject down to date. The concise, systematic treatment of the whole makes it a very convenient résumé of a subject of more than usual interest.

OBITUARY.

James Duncan Hague, long prominent as a mining engineer, died on August 5 at the age of seventy-two years. He was one of the geologists of the Survey of the 40th Parallel in 1867–70.

SUPPLEMENT.

Art. XXV.—*On the Esterification of Malonic Acid*; by I. K. Phelps and E. W. Tillotson, Jr.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxxi.]

Finkelstein* has shown that diethyl malonic ester may be prepared by dissolving malonic acid in the least possible amount of absolute alcohol before saturating with hydrochloric acid gas. The excess of alcohol is then distilled off, the residue poured into water, neutralized with sodium carbonate, and extracted with ether. On evaporation of the ether, diethyl malonic ester, boiling for the most part at 195°, is obtained. He gives no quantitative results. Conrad† has followed a precisely similar procedure, using the calcium salt of malonic acid instead of the acid itself. The yield given is 70 per cent of that theoretically possible. Quite recently Bogojawlensky‡, by boiling a solution of malonic acid in alcohol under a return condenser for six to seven hours, in the presence of anhydrous copper sulphate or potassium pyrosulphate as dehydrating agents, has obtained yields of malonic ester 68 per cent of that theoretically possible. In former papers§ from this laboratory studies of conditions giving high yields of the ethyl esters of succinic and benzoic acids have been made. And, further, the effect upon the quantity of ester produced, caused by varying three factors in the reaction, was shown. These factors were, first, the quantity of alcohol, second, certain catalyzers, and third, the period of the time of action. In this paper a similar study of the esterification of malonic acid with ethyl alcohol is recorded. For the preparation of pure malonic acid, the diethyl ester was purified by repeated fractional distillations under atmospheric pressure.‖ Portions of malonic ester,

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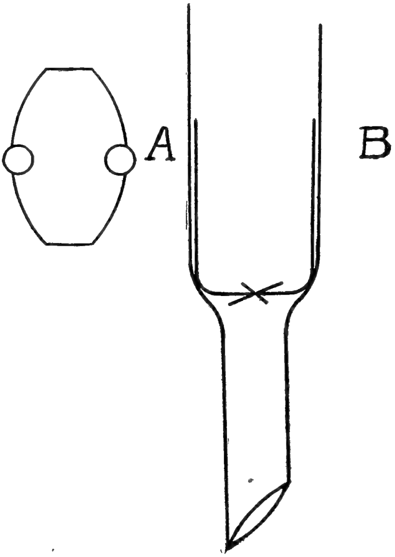
* Ann., cxxxiii, 338.

† Ibid., cciv, 126.

‡ Berichte, xxxviii, 3344.

§ This Journal, xxii, 368; xxiv, 194; xxv, 39.

‖ In distilling the ester, the following simple modification of the Hempel bead column was found advantageous. To the lower end of the column, which was 15^{mm} in diameter, was fused a glass tube 7^{mm} inside diameter and 5^{cm} long, the lower end of which was ground off at an angle. To prevent the beads from falling through this tube, two devices were made use of. Either A, shown by itself, or B, shown in position in such a column in the boiling within two-tenths of a degree, were hydrolyzed by heating at a temperature of about 50°, a mixture of ester and water in nearly equal amounts with a few drops of nitric acid, for some time after the mixture became homogeneous. The solution was then transferred to a porcelain dish and evaporated to the point of saturation at a temperature not exceeding* 60°, filtered while hot, and stirred while cooling. After recrystallizing from water, the acid was dried, first in the air, and then to constant weight in a desiccator over sulphuric acid. The malonic acid prepared in this manner was proved to be pure by titrating it against standard sodium hydroxide† and barium hydroxide solutions.



cut. A is a glass tube 1^{cm} in diameter, drawn together at either end, and held in place in the column by three " tears " fused to it. B is a small glass rod bent into a U shape wide enough to slip easily into the column. To the bottom of the U are fused one or more crosspieces of the same small glass rod, thus forming a grating which allows a ready escape for the vapors and the return of condensed liquid. The number of crosspieces necessary varies, obviously, with the internal diameter of the column and the size of the beads used. This device is also useful in connection with constricted side-necked flasks, since very little constriction is sufficient to hold it in place. The device can be varied for introducing a bead column in the side neck of a Claisen flask by lengthening the upright rods sufficiently for the device to be held in the angle of the side-neck tube. This modification obviates the necessity of constricting the neck in this case. Even in distilling high boiling point liquids like diethyl malonic ester, when the amount of liquid flowing back is large, liquid does not collect in such a column. In practice, B seems preferable to A on account of the more ready back flow of liquid.

[*] F. Lamouroux, Compt. Rend., cxxviii, 998.

[†] This Journal, xxvi, 138.

The alcohol used was the alcohol of commerce made as free as possible from water by repeated distillations over fresh calcium oxide. Pure zinc chloride of commerce was freshly fused and treated with a current of dry hydrochloric acid gas until a clear melt was obtained; then this mass was heated for a short time to expel any hydrochloric acid gas before cooling and granulating.

In every experiment recorded in Table I, weighed portions of malonic acid were treated with definite amounts of absolute alcohol, alone, or charged with a known amount of dry hydrochloric acid gas with or without a definite weight of zinc chloride, in the special arrangement of flasks described in a former paper for use in esterifying succinic* acid. In all experiments, except those in which the treatment was special, definite amounts of malonic acid with 40^{cm^3} of absolute alcohol, alone or charged with dry hydrochloric acid gas, or in presence of whatever other catalyzer was employed, were heated in a 500^{cm^3} round-bottomed flask, while the remainder of the alcohol used containing hydrochloric acid or not, as shown in the table, was boiled in a second 500^{cm^3} round-bottomed flask, and passed in vapor form to the bottom of the malonic acid solution in the first flask, which was kept at a temperature of 100° to 110° by heating in a bath of sulphuric acid and potassium sulphate. The temperature in the esterification flask was registered by a thermometer dipping into the alcoholic solution and held in place by a three-bored rubber stopper which carried the inlet tube, and also a Hempel bead column, arranged as described in the paper to which reference has been made, to provide an outlet for the vapors liberated in the flask.

The product obtained was transferred, with the aid of a small amount of ether, to a separating funnel containing chipped ice, and treated with an excess of an aqueous solution of sodium carbonate. The ethereal solution was washed with a solution containing sodium chloride. To recover traces of ester in the wash waters, the carbonate and chloride solutions were shaken out twice, successively, with fresh portions of ether, the ether extracts combined in a 250^{cm^3} side-necked flask fitted for vacuum distillation, with a capillary tube and receiver consisting of a 100^{cm^3} side-necked flask connected through a manometer to an aspirating pump. The low-boiling products, consisting chiefly of ether, alcohol and water, were removed by heating the flask containing the ester solution in a water bath, finally at a temperature of 60° for fifteen minutes after the manometer showed a pressure of 15^{mm}. The water bath was then replaced by an acid potassium sulphate bath, heated to about 140°, and the diethyl malonic ester distilled

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* This Journal, xxiv, 194.

and collected in the 100$^{cm^3}$ side-necked receiver, which was kept cool by allowing a stream of cold water to flow over it constantly.

In every experiment in Table I the flow of hot alcohol vapor was started into the malonic acid solution before the temperature reached 105°, which temperature was attained within fifteen minutes after beginning the experiment, and a steady current was maintained afterwards, holding the temperature between 100° and 110° till all the alcohol had been distilled

TABLE I.

No.	Malonic acid	$ZnCl_2$	Alcohol with HCl		Reaction time		Malonic ester		
	grm.	grm.	cm³.	per cent	hr.	min.	Theory grm.	Found grm.	per cent
(1)	50	--	200	--	1	50	76·92	54·00	70·2
(2)	50	--	200	1·25	1	--	76·92	65·02	84·5
(3)	50	--	200	1·25	1	45	76·92	68·53	89·1
(4)	50	--	300	1·25	2	30	76·92	72·39	94·0
			100	1·25	3	--			
			100	1·25	4	--			
(5)	50	--	200	1·25	2	--	76·92	72·06	93·7
			40	1·25					
(6)	50	0·5	160	--	-	55	76·92	65·22	84·0
(7)	50	1·0	200	--	-	40	76·92	36·13	47·0
			40	1·25					
(8)	50	1·0	160	--	-	45	76·92	69·45	90·3
			40	1·25					
(9)	50	1·0	160	--	-	45	76·92	64·17	82·6
			40	1·25					
(10)	50	1·0	160	--	1	40	76·92	66·94	87·0
(11)	50	1·0	200	1·25	-	45	76·92	69·02	90·0
(12)	50	1·0	300	1·25	-	50	76·92	71·25	92·7
			40	10					
(13)	50	1·0	260	--	1	10	76·92	67·93	88·3
			40	10					
(14)	50	1·0	260	--	2	30	76·92	68·67	89·3
			40	1·25					
(15)	50	10·0	160	--	-	35	76·92	67·07	87·2
			40	1·25					
(16)	50	10·0	160	--	1	50	76·92	68·67	89·3
(17)	50	10·0	200	1·25	-	45	76·92	71·39	92·8
(18)	50	10·0	200	10		55	76·92	62·11	80·8
(19)	50	10·0	200	10	1	30	76·92	58·10	75·5
(20)	50	10·0	400	1·25	1	50	76·92	70·30	91·4
			200	1·25	1	10			
(21)	50	10·0	200	1·25	1	15	76·92	67·31	87·5
			200	1·25	-	45			
(22)	50	10·0	200	1·25	-	55	76·92	71·71	93·2

over, except in experiments (5), (9), (10), (21) and (22), where the treatment was special. In experiment (5) the malonic acid, dissolved in the first portion of alcohol shown in the table, and contained in the 500^{cm^3} round-bottomed flask, was heated on a water bath at 50° for three hours, then connected with a vacuum pump and heated with the water bath at the same temperature until 40^{cm^3} of liquid, consisting, presumably, of water and alcohol, had distilled over. The second portion of alcohol was then added and the heating on the water bath at 50° continued for four hours, after which about 80^{cm^3} of liquid was removed under diminished pressure as before. Finally, 40^{cm^3} of the third portion of alcohol shown in the table was added and the process of esterification completed in the same manner as in the other experiments. In experiments (9) and (10) the current of alcohol vapor at first was slow; in the case of experiment (9), for fifteen minutes; in the case of experiment (10), for an hour, and more rapid for the remainder of the time. In experiment (21), after treatment in the usual manner with the first portion of alcohol, the low-boiling products were removed under diminished pressure by heating the esterification flask on a water bath at 60° till the manometer showed a pressure of 15^{mm} for fifteen minutes, and the process of esterification was repeated with the second portion of alcohol, shown in the table. In experiment (22) the malonic acid, zinc chloride and 200^{cm^3} of alcohol were boiled in the 500^{cm^3} round-bottomed flask under a return condenser for forty-five minutes before continuing the esterification with the second portion of alcohol in the usual manner.

To learn whether any ester had distilled with the alcohol during the esterification, several of the alcoholic distillates were cooled with ice diluted with three or four times its volume of water and shaken out separately three times with fresh portions of ether, washing the collected portion with a solution of sodium carbonate, and, finally, with pure water. The combined ether solutions were then fractioned *in vacuo* as described above. In no case was malonic ester found in the distillates tested. The loss inherent in the process employed for recovering the pure ester from the crude material, produced in the esterification flask, was determined by treating 75 grm. of pure malonic ester by the same procedure, described above, for the crude material. The loss amounted to 1·25 grm. of malonic ester.

From experiments (1), (2), (3) and (4) of Table I it is plain that an increase in either the amount of alcohol containing hydrochloric acid, or the time of action, gives an increase in the amount of ester produced. Comparing experiments (1) and (7), absolute alcohol alone, in the absence of zinc chloride, acting for a longer time, produces a far greater amount of ester than is obtained by the use of zinc chloride for a shorter time. However, if, as in experiment (8), a small amount of hydrochloric acid is present with the zinc chloride, the yield is increased 43 per cent over experiment (7) when zinc chloride was present but no hydrochloric acid, and 5·5 per cent over experiment (2), when hydrochloric acid was used with no zinc chloride. In experiment (11) the use of 1 grm. of zinc chloride with hydrochloric acid gives an increase of 5·5 per cent over experiment (2), where zinc chloride was not used. Comparing experiments (6), (8) and (15), it is apparent that under similar conditions, 1 grm. of zinc chloride gives better yields than 0·5 grm. or 10 grm. for the shorter time, while for a longer time, as shown in experiments (10) and (16), 10 grm. of zinc chloride seem to give the better yield. Increasing the amount of alcohol driven over in the same time, as shown in experiments (11) and (12), gives a decided increase in the amount of ester obtained, while increasing the amount of hydrochloric acid to 10 per cent tends to reduce the amount of ester formed, as is evident in experiments (18) and (19). In experiments (1) to (4) and in certain of the others, ethyl acetate was detected by its odor in the first few drops of the distillates, but when the esterification was partially completed on a water bath, as in experiments (5) and (22), before continuing in the regular apparatus, no ethyl acetate could be detected by its odor in the presence of the large mass of alcohol, and, in the case of experiment (22) a better yield of ester was obtained. It is possible that in experiment (5) some ester was lost during the treatments under diminished pressure, as described above.

For all the experiments in Table II, sulphuric acid of commerce sp. gr. 1·84, and commercial alcohol, made anhydrous by the method described, were used. In the experiments in series A, the procedure was precisely as in the experiments of Table I. In series B, malonic acid was treated with the first portion of alcohol and the small amounts of sulphuric acid, shown in Table II. This solution was boiled under a return condenser for one hour, then the second amount of sulphuric acid was added and the process of esterification completed with the second portion of alcohol in the usual manner. In series C, the procedure was the same as that described for experiment (5) of Table I. It was found in experiment (1) of series A that when malonic acid was treated in the esterification apparatus in the presence of sulphuric acid, there was a distinct odor of ethyl acetate in the distillate, indicating decomposition of the malonic acid, or the acid ester, but when the alcoholic solution was boiled under a return condenser for an hour, as in experiment (4) of series B, the odor of ethyl acetate was not observed. There was also some decomposition, as evidenced by the odor of ethyl acetate in the distillate of experiment (2) of series B, when the solution was heated immediately to 105° in the esterification apparatus, but if the temperature was kept at 90° for fifteen minutes, as in experiment (3) of series B, the ethyl acetate was not detected by its odor in the distillate in the presence of the large amount of alcohol. For the purpose of examining the distillates more closely for the presence of ethyl acetate, blank tests were made by mixing in a side-necked flask, connected with a condenser, a solution of alcohol and ethyl acetate with an equal volume of concentrated sulphuric acid, and heating the liquid to a temperature of 80°, at the same time passing a current of air through the liquid. About 3^{cm^3} of the distillate was collected in a graduated pipette, containing an aqueous solution of sodium chloride, and thoroughly shaken. When 50^{cm^3} of alcohol and $1{\cdot}8^{cm^3}$ of ethyl acetate, which was calculated as the least amount to be found in any of the distillates, if all of the malonic acid not found as ester had been decomposed, was treated in this manner, $0{\cdot}4^{cm^3}$ of liquid separated out, easily recognized by its characteristic odor as ethyl acetate. In treating by the process outlined above the first 50^{cm^3} of the alcoholic distillates of experiments (5) and (6) of series B and (1) and (2) of series C, no ethyl acetate could be detected.

In order to learn, if possible, whether the loss of malonic acid in the process of esterification was due entirely to decomposition, or whether part of the malonic acid was incompletely esterified, experiments were made to discover if malonic acid could be recovered from water solution. Shaking out a water solution containing sodium chloride and 2 grm. of malonic acid three times with ether gave 0·05 grm. of malonic acid, but when 5 grm. of malonic acid, in a similar solution, were treated eighteen hours in an ether extractor, and the ethereal solution evaporated under diminished pressure at 60° until the manometer registered 15^{mm}, 4·97 grm. were recovered. A blank test on 5 grm. of pure malonic acid showed no loss in drying from an aqueous ether solution at 60° *in vacuo.* The sodium carbonate wash waters were acidified with hydrochloric acid and treated for eighteen hours in an extractor similar to that described by Van Rijn*, except that an ordinary test tube of about 100^{cm^3} capacity was used instead of the constricted and perforated tube employed by him. The amounts of malonic acid so recovered are shown in Table II. The amount of malonic ester taken up by the sodium carbonate wash waters was determined by a blank test on 75 grm. of pure malonic ester, which was treated with a sodium carbonate solution, as

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* Berichte, xxviii, 2387.

described for the recovery of malonic ester. Upon acidifying this sodium carbonate solution with hydrochloric acid and treating in the extractor as outlined above, 0·30 grm. of malonic acid equivalent to 0·39 grm. of ester was obtained.

In calculating the figures given in the last column that stand for the per cent of malonic acid, or ester, unaccounted for, it was considered fair to add to the amount of malonic ester obtained in a single experiment 1·25 grm., the amount found by the blank test to be the loss inherent in the process of recovery of the pure ester. To this sum was added the amount of ester equivalent to the difference between the malonic acid obtained from the sodium carbonate wash waters and 0·39 grm., which as has been shown is the fraction of the

TABLE II.

					Malonic ester			Malonic acid	
No.	Malonic acid grm.	Alcohol cm³.	H_2SO_4 grm.	Time hr. min.	Theory grm.	Found grm.	Per cent	Found in wash water grm.	Not accounted for per cent
					A				
		40	2·00						
1	50	160	---	1 – 15	76·92	70·96	92·30	---	--
					B				
		100	0·15	1 – 00					
1	50	200	---	1 – 00	76·92	67·62	87·90	1·66	7·8
		60	0·15	1 – 00					
2	50	140	1·85	1 – 00	76·92	70·00	91·00	1·04	5·8
		100	0·15	1 – 00					
3	50	200	1·85	0 – 45	76·92	70·84	92·09	1·05	4·8
		100	0·15	1 – 00					
4	50	200	1·85	1 – 00	76·92	71·50	92·95	---	--
		100	0·15	1 – 00					
5	50	200	1·85	2 – 00	76·92	73·12	95·06	0·36	3·2
		100	0·15	1 – 00					
6	50	300	1·85	2 – 35	76·92	72·60	94·38	0·37	3·9
		100	0·15	1 – 00					
7	50	200	4·85	1 – 00	76·92	70·93	92·21	1·80	3·2
					C				
		100	0·15	3 – 00					
		100	---	4 – 00					
		50	1·85	-----					
1	50	200	---	2 – 00	76·92	73·67	95·77	0·39	2·4
		100	2·00	4 – 00					
		100	---	4 – 00					
		50	---	-----					
2	50	200	---	2 – 00	76·92	73·94	96·11	0·40	2·1

1·25 grm. loss in the process of recovery, taken up by the sodium carbonate water, and recovered as malonic acid by the ether extraction. Taking, for example, experiment (2) of series C in Table II, of the 0·40 grm. of malonic acid recovered from the wash water, 0·30 grm. was presumably due to the action of the sodium carbonate on the ester during the process of shaking out with ether. We have then, 73·94 grm. of ester found, 1·25 grm. of ester lost during the process of recovering the ester and acid, corresponding to 0·13 grm. of ester, remaining unesterified. The total, therefore, of ester accounted for is 75·32 grm. or 97·9 per cent, leaving 2·1 per cent lost, probably through decomposition. In this particular experiment, as well as in experiment (1) of series C, a part of the loss is due to vaporization of ester during the interpolated treatments under diminished pressure.

From the results shown in Table II it is evident that under conditions which give the best yield, not more than 0·10 grm. of malonic acid remains unesterified, and, further, that about 1 grm. or two per cent of acid is lost through decomposition. Under conditions less favorable for theoretical yields, a larger amount of acid remains unesterified, and at the same time the amount lost by decomposition is greater. Comparing experiments (2) and (3) of series B, it is evident that increasing the amount of alcohol with which the malonic acid is treated on the water bath, from 60^{cm^3} to 100^{cm^3}, increases the yield by one per cent, while if malonic acid is treated with several portions of alcohol as described above, and shown in experiments (1) and (2) of series C, or if the time of driving over the second portion of alcohol is increased as in experiment (5) of series B, a much larger yield of ester is obtained. Merely increasing the amount of alcohol distilled over, as in experiment (6) of series B, gives no better yield than under otherwise similar conditions in experiment (5). In experiments (1), (4) and (7) it is plain that with small amounts of sulphuric acid, esterification is not complete, while with larger amounts the yield of ester is apparently not quite as good as that produced by two grams. By varying the time in experiments (3), (4) and (5) of series B, a larger yield of ester is obtained, with increase in the time taken to distil the second portion of alcohol, while if the alcoholic solution of malonic acid is heated for a longer time on the water bath, as in experiments (1) and (2) of series C, the yield is materially increased.

The ester obtained in all the experiments of Tables I and II was found to be in a high state of purity, since, on redistillation, it showed no considerable variation in boiling point.

From the work here described, it may be seen that in general, increasing within limits the amount of alcohol used, and the time during which it is allowed to act, produces a more complete esterification of malonic acid. Larger amounts of zinc chloride up to 10 grm. appear to increase the yield as in experiments (1), (4) and (17) of Table I, while the use of 5 grm. of sulphuric acid seems to possess no advantage over 2 grm., as is shown in experiments (4) and (7) of series B in Table II. Under similar conditions, however, 2 grm. of sulphuric acid with 200^{cm^3} of absolute alcohol running for one hour and fifteen minutes in experiment (1) of series A in Table II gives a yield of malonic ester nearly equal to that produced by 1 grm. of zinc chloride and 300^{cm^3} of alcohol, charged with 1·25 per cent hydrochloric acid and running for 50 minutes, in experiment (12) of Table I, or to that produced in experiment (17) of Table I by 10 grm. of zinc chloride and 200^{cm^3} of alcohol charged with 1·25 per cent hydrochloric acid.

Finally it has been shown that by allowing malonic acid and absolute alcohol to react in the form of apparatus described, a yield of malonic ester, equal to the best described in the literature, may be obtained, while by treating for a long time with alcohol charged with hydrochloric acid increases the yield over twenty per cent. The presence of sulphuric acid or of zinc chloride and alcohol charged with hydrochloric acid permits the action to proceed in a shorter time. The best yields of malonic ester were obtained by causing the esterification to proceed as far as possible at a temperature below that at which the malonic acid decomposes. This was accomplished, as described above, by heating an alcoholic solution of malonic acid with sulphuric acid on a water bath at 50° for eight hours, and treating the residue obtained in this manner with a fresh portion of alcohol for a period of two hours. By following this procedure, a yield of 96·1 per cent of malonic ester was obtained, with only 2·1 per cent lost, either through decomposition of the acid, or acid ester, or by volatilization of the ester.

ART. XXVI.—*Concerning the Purification of Esters;* by I. K. and M. A. PHELPS and E. A. EDDY.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxxii.]

QUANTITATIVE studies of the ester reaction were made under the direction of one of us and published earlier in this Journal.* In that work the exactness was shown with which in the preparation of the ethyl esters of succinic, malonic and benzoic acids, the crude product of esterification obtained in the special form of apparatus used, may be treated to isolate the pure ester. In brief this treatment consisted in shaking out the crude ester with ether, in the presence of an excess of sodium carbonate in solution, distilling off under diminished pressure the low boiling point products, and, finally, the ester which was collected and weighed. This method of purifying esters is a modified form of the procedure in common use for isolating a pure ester from the crude product obtained during esterification. Others† have separated by distillation under diminished pressure the water taken up by the ether during the shaking out of the crude ester from the sodium carbonate solution. This method of removing the water at as low a temperature as possible, so that hydrolysis may not take place, is particularly adapted for use in a quantitative study of the ester reaction. The organic acid unesterified and the mineral acid used as a catalyzer is commonly removed by treatment with sodium or potassium carbonate. Where the esters are soluble in water Fischer and Spier‡ varied the procedure by treating the crude product from esterification with an excess of pulverized potassium carbonate, and removed, after long shaking, the potassium salt by treatment with ether. The filtrate was freed from ether on a water bath and fractionated under diminished pressure.

A study is given here of the exactness with which dry potassium carbonate may be used in isolating succinic, malonic and benzoic ethyl esters impure with alcohol, water, unesterified organic acid and small amounts of mineral acid. For this purpose mixtures of the purified esters were made with the substances, as shown in the table, and the ester separated and weighed.

Definite portions, 75 grm. each, of carefully purified diethyl succinate, diethyl malonate, or ethyl benzoate were placed in a Claisen flask of 250$^{cm^3}$ capacity, chilled in ice, together with 2 grm. of the corresponding acid, 2$^{cm^3}$ of concentrated hydro-

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* This Journal, xxiii, 368; xxiv, 294; xxv, 39; xxvi, 143.

† J. Am. Chem. Soc., xxiii, 1105, 1896.

‡ Berichte, xxviii, 3252.

chloric acid of commerce or 1$^{cm^3}$ of concentrated sulphuric acid of commerce, 10$^{cm^3}$ of alcohol nearly absolute and an excess—10 grm.—of either pure potassium carbonate of commerce or the same freshly fused and cooled before introducing into the ester mixed with impurities. These impurities are present here in larger proportion than would be expected if the ester were produced according to the procedure referred to earlier in this paper. The Claisen flask was connected for distillation under diminished pressure with a second Claisen flask of 100$^{cm^3}$ capacity used as a receiver. To secure a current of air through the apparatus during the entire operation an open glass tube was used in place of the usual capillary tube. The 100$^{cm^3}$ Claisen was connected either directly or with a glass tube held through a rubber stopper to the larger Claisen, the side neck of which was very short, in the same manner as has been described in a former paper* for the distillation of a substance where loss of some of it in the side neck of the flask might otherwise be expected. The 250$^{cm^3}$ flask was then heated under diminished pressure by means of an acid potassium sulphate bath at a temperature of 100°–110° for about an hour, or until no further evolution of carbon dioxide indicated that the acid was completely neutralized, while at the same time a current of water was allowed to strike the receiver constantly during neutralization to condense all products possible. The temperature of the acid bath was then raised and the ester carefully distilled into the receiver, taking care by raising the temperature of the bath and flaming to remove the final traces of the ester held on the side wall of the flask. The contents

						Ester	
No.	Alcohol cm^3.	HCl cm^3.	H_2SO_4 cm^3.	K_2CO_3 grm.	Organic acid 2 grm.	75 grm.	Recovered grm.
(1)	10	2		10	Succinic	Succinic	74·40
(2)	10	2		10	Succinic	Succinic	74·67
(3)	10		1	10	Succinic	Succinic	74·41
(4)	10		1	10	Succinic	Succinic	74·56
(5)	10	2		10	Malonic	Malonic	74·24
(6)	10	2		10	Malonic	Malonic	74·20
(7)	10		1	10	Malonic	Malonic	74·31
(8)	10		1	10	Malonic	Malonic	74·27
(9)	10	2		10	Benzoic	Benzoic	74·55
(10)	10	2		10	Benzoic	Benzoic	75·00
(11)	10		1	10	Benzoic	Benzoic	74·60
(12)	10		1	10	Benzoic	Benzoic	74·67

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* This Journal, xxiv, 479.

—ester, alcohol and water—of the second 100^{cm^3} Claisen flask, connected in the manner just given for distilling under diminished pressure, were carefully fractionated by heating the Claisen flask in a water bath raised slowly to 60°, which temperature was maintained for 15 minutes after the manometer showed a pressure of 15^{mm}, and the ester distilled in the usual manner into the flask, weighed, in some instances, alone, in others, with the short tube held in place during distillation by the rubber stopper, and the weight of ester determined.

In all the experiments in the table except (3), (4), (8) and (10) the potassium carbonate was ignited before attempting to neutralize the esters mixed with organic and mineral acids. In experiments (3), (4), (7), (8), (9) and (10), both in distilling and redistilling the ester from the Claisen flasks the process was carried out in flasks where the shortened side-neck tube of the first flask was held with a glass tube through a rubber stopper. It seems evident that igniting freshly the potassium carbonate is unnecessary. Further, the jointed apparatus does not appear to diminish the small loss of ester.

The purity of the product obtained was shown by redistilling the recovered ester at atmospheric pressure, when it was found that the entire portion distilled within a fraction of a degree.

From an inspection of the results obtained it is clear that diethyl succinate, diethyl malonate and ethyl benzoate may be freed from small amounts of mineral and organic acids, when alcohol is present, by heating suitably with dry potassium carbonate under diminished pressure, and that the total product obtained in this way, fractionated under diminished pressure, gives a satisfactory indication that ester is not lost in considerable amounts. The losses in the treatment of the masses of 75 grm. each of pure ester as in the former work from this laboratory, referred to above, amounted to 0·6 grm. in the case of the recovery of succinic ester, to 1·25 grm. in the case of malonic ester, and to 0·25 grm. in the case of benzoic ester. While the loss in the recovery of ethyl benzoic ester by neutralizing as described with dry potassium carbonate is slightly greater than by shaking out with ether, the loss in recovering diethyl succinic ester is somewhat less, and the loss in recovering diethyl malonic ester is much less than by shaking out with ether. But, even in the case of ethyl benzoic ester, the treatment with dry potassium carbonate is to be preferred of the two procedures, both on account of the greater ease in manipulation and on account of the saving in expense, since dry potassium carbonate accomplishes the purpose of the aqueous sodium carbonate and shaking out with ether.

Obviously it is possible to neutralize the acid impurities present with these esters with dry potassium carbonate completely and advantageously. It is easy to see, however, that the smaller the amounts of free acid, the more completely can the total amount of ester present be recovered. With such amounts of unesterified acid as remain when organic acids are treated with alcohol containing mineral acid, on a return condenser, according to Fischer, the loss of ester might be considerable. But with such amounts of free acid as are left when esters are made in the special form of apparatus described in a former paper, neutralizing in the manner given here with dry potassium carbonate is easily done without loss of ester in considerable amount. This is obviously true, since in the mixtures shown in this paper the esters contain acid impurities far in excess of the amount that would be found when esterifying under proper conditions for ideal yields.

ART. XXVII.—*On the Conversion of Cyanacetic Ester to Malonic Ester;* by I. K. PHELPS and E. W. TILLOTSON, JR.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxxiii.]

KOLBE* and Müller†, in synthesizing the acids of the oxalic acid series from derivatives of the acetic acid series, note that if cyanacetic acid or its ester is boiled with a concentrated solution of potassium hydroxide, potassium malonate is obtained. This treatment with potassium hydroxide was followed by Finkelstein‡, Franchimont§, Von Miller‖ and Conrad¶, but in no case were the quantities obtained given. Van't Hoff**, starting with cyanacetic acid, states that the yield of malonic acid obtained by this process is eighty per cent of that theoretically possible. He explains the loss as due to decomposition according to this equation :

$$CH_2(COOK)_2 + KOH = CH_3COOK + K_2CO_3.$$

Franchimont†† and Van't Hoff†† both give it as their opinion that a better yield may be obtained by the use of hydrochloric acid in the place of potassium hydroxide as a hydrolizing agent. Hydrochloric acid was apparently first made use of for the purpose of converting cyanacetic acid to malonic acid by Grimaux and Tchierneak‡‡, later by Bourgoin§§, and by Claisen and Venable‖‖. Noyes¶¶ employed sulphuric acid in the presence of chlorides to effect the same conversion, but in none of the instances cited were the quantities obtained given to show the amount of malonic acid or ester obtainable from a given amount of cyanacetic acid or ester.

For the work here recorded, cyanacetic ester was made by esterifying the acid obtained by acting on chloracetic acid with potassium cyanide under conditions which will be given in a later paper. The cyanacetic ester, synthesized in this way, was fractionally distilled at atmospheric pressure with a Hempel bead column of the particular form described in a former paper*** in this Journal. The portions boiling within limits of four-tenths of a degree, 205·6°–206° (corrected), were used in all the experiments of series A in Tables I and II. During the distillation under atmospheric pressure, the ester in the flask assumed a deep red color, gradually depositing a small

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* Ann., cxxxi, 348.

† Ann., cxxxi, 350.

‡ Ann., cxxxiii, 338.

§ Berichte, vii, 217.

‖ Jour. Prakt. Chem. [2], xix, 326.

¶ Berichte, xii, 749.

** Berichte, vii, 1382.

†† Loc. cit.

‡‡ Bull. Soc. Chim., xxxi, 338.

§§ Comptes Rendus, xc, 1289.

‖‖ Ann., ccxviii, 131.

¶¶ Jour. Am. Chem. Soc., xviii, 1105.

*** This Journal, xxvi, 243.

amount of a reddish-brown insoluble substance. The ester obtained in this manner gave the following analyses:

I. 0·3252 grm. of ester gave $30·5^{cm^3}$ of moist nitrogen at 24° and $758·2^{mm}$. N = 10·48 per cent.
II. 0·4891 grm. of ester gave $45·8^{cm^3}$ of moist nitrogen at 25° and 774^{mm}. N = 10·45 per cent.
Calculated for $C_5H_7O_2N$, N = 12·40 per cent.

For the experiments in series B of Tables I and II the cyanacetic ester was fractionally distilled under diminished pressure and was proved by the following analyses to be pure:

I. 0·5020 grm. of ester gave $55·3^{cm^3}$ of moist nitrogen at 23° and $763·2^{mm}$. N = 12·47 per cent.
II. 0·5004 grm. of ester gave 55^{cm^3} of moist nitrogen at 20° and $758·2^{mm}$. N = 12·54 per cent.
Calculated for $C_5H_7O_2N$, N = 12·40 per cent.

The alcohol used in all the experiments recorded was made as free as possible from water by repeated distillations from calcium oxide. Zinc chloride of commerce was freshly fused for use in the experiments of Table I. In the experiments of Table II sulphuric acid of commerce, sp. gr. 1·84, was employed.

In all the experiments in Tables I and II, except those in which the treatment was special, 50 grm. of cyanacetic ester, contained in a 500^{cm^3} round-bottomed flask, together with definite amounts of absolute alcohol, zinc chloride or sulphuric acid, and with or without definite amounts of water, as shown in the tables, were saturated with gaseous hydrochloric acid, dried by passing through a wash bottle containing concentrated sulphuric acid, keeping the solution cooled in a mixture of ice and salt. While the current of hydrochloric acid was still flowing, the ice mixture was replaced by means of a water bath, and the solution heated to the boiling point of the alcohol under a reflux condenser for an additional period of time, as shown in the tables.

The ammonium chloride was filtered off and washed with absolute alcohol or ether. The filtrate was then treated in the special arrangement of flasks for esterification described in a former paper* in this Journal. For this treatment, 200^{cm^3} of absolute alcohol was distilled from the reservoir flask through a period of one and one-half to two hours. The crude product so obtained was transferred to a separating funnel containing chipped ice, an excess of sodium carbonate solution added to neutralize any free acid present, and the whole shaken out with ether. The ethereal solution was washed with water containing sodium chloride, and the carbonate and chloride

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* This Journal, xxiv, 194.

TABLE I.

					Hydrochloric acid		Malonic ester		
No.	Cyanacetic ester grm.	$ZnCl_2$ grm.	C_2H_5OH mols.	H_2O mols.	cold hr.	hot hr.	Theory grm.	Found grm.	Per cent
					A				
(1)	50	1	5	1	4	2	67·61	61·20	90·5
(2)	50	1	5	2	4	2	67·61	60·95	90·1
(3)	50	10	5	0	4	3	67·61	64·59	95·5
(4)	50	10	5	0	4	0	67·61	64·88	96·0
(5)	50	10	5	0	5	0	67·61	38·31	56·6
					B				
(1)	50	0	5	0	4	0	70·80	67·15	94·8
(2)	50	0	5	0	0	2·5	70·80	66·05	93·3
(3)	50	10	5	0	4	2	70·80	66·25	93·5

TABLE II.

					Hydrochloric acid		Malonic ester		
No.	Cyan-acetic ester grm.	H_2SO_4 grm.	C_2H_5OH mols.	H_2O mols.	cold hr.	hot hr.	Theory grm.	Found grm.	Per cent
					A				
(1)	50	110	4·5	1	0	3	67·61	52·00	77·0
(2)	50	2	5	1	4	2	67·61	63·72	94·2
(3)	50	2	5	1	11	5	67·61	63·30	93·6
(4)	50	2	5	2	4	2	67·61	61·85	91·5
(5)	50	2	10	2	5	2	67·61	55·84	82·5
(6)	50	2	10	2	10	2	67·61	59·64	88·2
(7)	50	4	5	0	4	0	67·61	64·96	96·0
(8)	50	4	5	0	4	2	67·61	64·79	95·8
(9)	50	4	5	1	4	2	67·61	65·61	97·0
(10)	50	4	10	2	8	2	67·61	57·22	84·6
					B				
(1)	50	4	5	0	4	0	70·80	68·21	96·3
(2)	50	4	5	0	4	2	70·80	66·92	94·5
(3)	50	4	5	0	0	2	70·80	64·82	91·5

wash waters were shaken out successively with two fresh portions of ether. The combined ethereal solutions of the ester were separated from low boiling impurities, distilled under diminished pressure in the usual manner, and the ester weighed. The malonic ester obtained was found to be pure, since it showed no considerable variation in boiling point.

In experiments (3) of series A and (3) of series B of Table I, (8) of series A and (2) of series B of Table II, the filtration and process of esterification were omitted. Enough water was added to dissolve the ammonium chloride and the ester was recovered directly in the manner described above. In experiments (4) of series A, (1) of series B of Table I, (7) of series A and (1) of series B of Table II, after saturation with hydrochloric acid in the cold, the solution was treated directly in the esterification apparatus, the ammonium chloride being precipitated when the temperature had reached 60°–70° during the process of esterification. In experiment (5) of series A of Table I, after saturating in the cold with hydrochloric acid, the excess of hydrochloric acid, alcohol, water and all low-boiling products were removed by heating the flask in a water bath at 50° under diminished pressure, and the remainder was esterified in the usual manner. In this experiment, no considerable amount of ammonium chloride was precipitated, and there remained in the distillation flask a viscous fluid which did not distil with the malonic ester and which began to decompose on being heated to a higher temperature. In experiment (1) of series A of Table II, cyanacetic ester was boiled with alcohol sp. gr. 0·825 and sulphuric acid sp. gr. 1·84 under a return condenser for two hours. and as no ammonium salt was precipitated, gaseous hydrochloric acid was passed in for three hours, the ammonium salt filtered off, and the process continued in the usual manner.

The theory for malonic ester given in series A of Tables I and II was calculated on the basis of the analyses of the first sample of ester, given above, and with the assumption that the substance was a mixture of cyanacetic and malonic esters. This assumption was apparently justified, first, by the fact that, on treatment, it yielded pure malonic ester, and second, on saponification, a mixture of cyanacetic and malonic acids was obtained. It was further assumed that all fractions prepared in the same way and boiling at the same temperature, 205·6°–206° (corrected), had the same composition. Experiments (7) and (8) of series A of Table II were made using portions of the samples analyzed. The theory given in series B of both tables was calculated on the basis of pure ethyl cyanacetate. This is presumed to be justified by the analyses given above as well as by the yields of malonic ester obtained from it.

The loss sustained by saturating an alcoholic solution of malonic ester with hydrochloric acid was determined by a blank test. When 75 grm. of pure ethyl malonate, with 125^{cm^3} of absolute alcohol was saturated with hydrochloric acid for the same time and under the same conditions as in the several experiments, 72·02 grm. were recovered, with a loss of 2·98 grm. or 4·2 per cent. This loss must be added to the results given in the table in order to show the extent of the conversion by this procedure. From the results given in Table I it is plain that with small amounts of zinc chloride as catalyzer, in the presence of one or two molecules of water, malonic ester may be obtained to the extent of 90 per cent of that theoretically possible, as shown in experiments (1) and (2) of series A. Taking into consideration the loss inherent in the process, we have 94 per cent accounted for. The loss of 6 per cent is doubtless due to decomposition of malonic ester or acid ester in the presence of water and the large amount of hydrochloric acid. When no water was used, as in the remaining experiments of the table, a much larger yield was obtained. Under these circumstances the water necessary for the conversion may have been formed in the secondary reaction between the alcohol and hydrochloric acid in the presence of the catalyzer, water and ethyl chloride being formed. The presence of ethyl chloride was detected in the alcoholic distillates from these experiments. It is also possible that the reaction took a different course, the imido ester hydrochloride first formed reacting with alcohol to form ammonium chloride and the ortho ester which, in the presence of the large amount of alcohol and the catalyzers, was easily decomposed with the formation of the normal ester and ethyl ether. This same sort of a reaction has been described by Claisen* in the case of acetals, which he finds are easily broken up by catalyzers with the formation of the aldehydes and ether. It is evident from the results obtained in experiments (1) and (2) of series B that the conversion of cyanacetic ester to malonic ester has been nearly quantitative, either because sufficient water has been formed in the secondary reaction mentioned above, or a reaction similar to that pointed out by Claisen has taken place, with the formation of ethyl ether, or both of these actions have gone on simultaneously. That is to say, the water theoretically demanded by the equation for the conversion of cyanacetic ester to malonic ester need not be introduced as such when the conversion is effected by hydrochloric acid in alcoholic solution. Since this is true and since malonic ester is so easily hydrolyzed, the better yields obtained without the use of any water are easily understood.

Experiment (4) of series A, which was treated in the esterification apparatus in order to complete the esterification of any acid ester that might have been formed, if too much water were present for any reason, shows a slight increase in yield over experiment (3) of series A, which was shaken out directly after saturation with hydrochloric acid and treatment on the return condenser. In experiment (5) of series A, after saturating in the cold with hydrochloric acid, the excess

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* Berichte, xl, 3903.

of water, alcohol, hydrochloric acid and all low-boiling products were removed under diminished pressure by heating the flask with a water bath at 50°. The residue, consisting, presumably, of imido ester hydrochloride, was then treated on the esterification apparatus as described above. The result indicates that, if hydrochloric acid is not present in sufficient amount, ethyl alcohol at a temperature of 100°–110° does not complete the reaction, while if large amounts of hydrochloric acid are present as in the other experiments of the table, the reaction proceeds at a temperature of 60°–70°. Experiment (2) of series B, which was treated with hydrochloric acid at the boiling temperature of the alcohol, shows not quite so good a yield as experiment (1) of series B, which was first saturated in the cold. The presence of large amounts of catalyzers in experiment (3) of series B produces a lower yield than that obtained in experiment (1) of series B, possibly through the formation of larger amounts of water and subsequent decomposition of malonic ester.

The experiments in Table II, in which sulphuric acid was used as a catalyzer, show the same general results as those of Table I. Better yields are obtained when no water is added, as in experiments (7) and (8) of series A and (1), (2) and (3) of series B, than in the remaining experiments where water was used. In experiment (1) of series A, sulphuric acid alone produced no apparent conversion to malonic ester at the temperature of a water bath, but when hydrochloric acid was passed in, the ammonium salt was precipitated and malonic ester was formed. Experiment (7) of series A, which was esterified after saturation, shows a slightly better yield than experiment (8) of series A, which was shaken out directly after saturation and treatment on the return condenser. In series B the difference is more marked in the case of experiments (1) and (2), respectively, which were similarly treated. In experiment (3) of series B, in which the gaseous hydrochloric acid was passed into a boiling alcoholic solution, the yield is much lower than in experiments (1) and (2) of series B, which were first saturated in the cold.

The work here recorded has shown that the conversion of cyanacetic ester to malonic ester is apparently not effected at the temperature of a water bath by sulphuric acid, and that in the absence of large amounts of hydrochloric acid it proceeds slowly, if at all, at 110°. However in the presence of large amounts of hydrochloric acid, with or without additional catalyzers, the reaction proceeds rapidly at the temperature of the boiling alcoholic solution. It has been shown that, in the presence of one or two molecules of water, high yields of malonic ester may be obtained, but that better yields result if no water is added as such, in which case sufficient water is formed in a secondary reaction or else the ortho ester first formed is decomposed into the normal ester and ethyl ether. High yields may be obtained without the use of a catalyzer other than the hydrochloric acid with which the solution was saturated, but by the use of an additional catalyzer as zinc chloride, or preferably sulphuric acid, nearly theoretical yields of malonic ester result. In experiment (7) of series A and (1) of series B in Table II, if the loss of 4·2 per cent sustained by the treatment and the recovery of the malonic ester, in the amount used here and under these conditions, is considered, it seems probable that the conditions named above are those under which conversion of ethyl cyanacetate to ethyl malonate is complete. The best results were obtained when 50 grm. of cyanacetic ester with 125$^{cm^3}$ of absolute alcohol and 4 grm. of sulphuric acid, cooled in a mixture of ice and salt, were thoroughly saturated with hydrochloric acid by passing in a stream of dry hydrochloric acid for four hours, the resulting mixture being esterified during a period of two hours, at 100°–110°, with 200$^{cm^3}$ of absolute alcohol. Under these conditions the yield actually obtained was 96·3 per cent of that theoretically possible.

ART. XXVIII.—*Researches on the Influence of Catalytic Agents in Ester Formation. On the Esterification of Cyanacetic Acid;* by I. K. PHELPS and E. W. TILLOTSON, JR.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxxiv.]

VAN'T HOFF* states that cyanacetic ester may be obtained by dissolving cyanacetic acid in alcohol, saturating with hydrochloric acid gas, pouring the mixture into water and extracting with ether, but he gives no data concerning the amount of ester to be obtained from a known amount of cyanacetic acid. In former papers† from this laboratory there have been shown the effects produced upon esterification of succinic, benzoic and malonic acids by varying the proportion of the reagents, the catalyzers and the time of reaction. In this paper is recorded a similar study with cyanacetic acid.

Cyanacetic ester was prepared from chloracetic acid under conditions which will be described in a later paper. The ester boiling within four-tenths of a degree, was converted to the acid by heating with double its volume of water and a few drops of nitric acid, at a temperature of about 60°, for some time after the mixture had become homogeneous. The solution was then evaporated at a temperature of 60° till the point of saturation was reached and the crystals which separated on cooling were recrystallized from a mixture of ether and chloroform. The acid so obtained was in the form of very fine, perfectly white, hygroscopic crystals, melting at 66·1–66·4° (corrected).

TABLE I.

No.	Cyanacetic acid grm.	$ZnCl_2$ grm.	H_2SO_4 grm.	Alcohol with HCl cm³	Alcohol with HCl per cent	Time hr.	Time min.	Cyanacetic ester Theory grm.	Cyanacetic ester Found grm.	Cyanacetic ester Per cent
(1)	50	--	--	40 160	--- ---	1	5	66·47	42·19	63·5
(2)	50	--	--	40 160	1·25 1·25	1	10	66·47	58·92	88·6
(3)	50	1	--	40 160	1·25 1·25	1	10	66·47	59·69	89·8
(4)	50	10	--	40 160	1·25 1·25	1	5	66·47	63·18	95·1
(5)	50	10	--	40 160	1·25 1·25	1	--	66·47	55·53	83·5
(6)	50	--	0·5	40 160	--- ---	1	10	66·47	62·68	94·3
(7)	50	--	2·0	40 160	--- ---	1	5	66·47	64·20	96·6
(8)	50	--	2·0	40 160	--- ---	2	10	66·47	64·52	97·1

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* Berichte, vii, 1382.

† This Journal, xxiv, 194; xxv, 39; xxvi, 143.

This acid, when neutralized with ammonium hydroxide, gave no precipitate with lead nitrate, indicating that no malonic or glycollic acid was present, and on analysis proved to be pure.

I. 0·4000 grm. gave 59·5$^{cm^3}$ moist nitrogen at 25° and 756·8^{mm}. N = 16·51 per cent.

II. 0·2910 grm. gave 43·1$^{cm^3}$ moist nitrogen at 25° and 762·1^{mm}. N = 16·57 per cent.

Required for $C_3H_3O_2N$, N = 16·48 per cent.

The alcohol was made as anhydrous as possible by repeated distillations over calcium oxide. For experiments (2) to (5) inclusive, absolute alcohol obtained as described above was charged with dry hydrochloric acid gas in the proportions of ten grams of hydrochloric acid per liter of alcohol. Pure zinc chloride of commerce, freshly fused, and sulphuric acid, sp. gr. 1·84, were used also as catalyzers.

In all of the experiments recorded in the table, fifty grams of cyanacetic acid with 40$^{cm^3}$ of alcohol, alone or charged with hydrochloric acid in the proportions already given, together with a definite weight of zinc chloride or sulphuric acid, were heated to a temperature of 100°–110°, using the special arrangement of flasks for esterification and the procedure for recovery of the pure ester, described in a former paper.*

The error inherent in the process was determined by treating 70 grm. of pure cyanacetic ester with 4 grm. of sulphuric acid and alcohol in the esterification apparatus, under the same conditions as in the several experiments, and recovering in the same manner. Under these conditions 68·33 grm. were recovered. Thus the results shown in the table must be approximately 2·5 per cent lower than the amounts of cyanacetic ester actually formed.

From experiment (1) it appears that with absolute alcohol, using no catalyzer, 63·5 per cent of cyanacetic ester may be obtained, but if the alcohol be charged with 1·25 per cent of hydrochloric acid, as in experiment (2), the yield is increased 25 per cent. In experiment (3) the addition of one gram of zinc chloride raises the yield one per cent over that of experiment (2) where no zinc chloride was used, and the presence of 10 grm. of zinc chloride further increases the yield to 95·1 per cent of cyanacetic ester actually obtained. In all the experiments in which alcohol charged with hydrochloric acid was used, a small amount of ammonium chloride, possibly 0·1 grm., separated during the treatment at 100°–110°, showing partial conversion to malonic ester. In experiment (5) no ammonium chloride was observed when the esterification was performed at 85°–90°, but under these conditions the yield of cyanacetic

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* This Journal, xxiv, 194.

ester was much lower. Similarly, in experiments (6), (7), and (8) in which sulphuric acid and absolute alcohol were used, no ammonium salt was precipitated and the ester obtained was evidently pure ethyl cyanacetate. In experiment (6) half a gram of sulphuric acid produces an increase of 31 per cent over experiment (1) in which conditions were the same, except that no catalyzer was present. Two grams of sulphuric acid in experiment (7) further increases the yield to 96·6 per cent, and by increasing the time to two hours, as in experiment (8), 97·1 per cent of cyanacetie ester was obtained. Taking into consideration the 2·5 per cent loss inherent in the process, it seems probable that the cyanacetic acid was completely esterified under the conditions imposed in experiment (8).

The work recorded here has shown that, using alcohol alone, with no catalyzer, 63 per cent of cyanacetic ester may be easily obtained, that the yield is increased by the use of catalyzers and, within limits, increases with the amount of catalyzer used. Increasing the time, as shown in one experiment, also causes a more complete esterification. The use of alcohol containing only 1·25 per cent of hydrochloric acid causes a partial conversion to malonic ester at 100°–110°, while with sulphuric acid as a catalyzer this reaction apparently does not take place. Esterification is more complete when sulphuric acid and absolute alcohol are used instead of zinc chloride and alcohol charged with hydrochloric acid, and nearly theoretical yields may be obtained by using two grams of sulphuric acid with 200^{cm^3} of absolute alcohol acting for a period of two hours. Hence, in the preparation of cyanacetic ester, hydrochloric acid may not be used if the temperature is above 100°. If the temperature is lower and if the concentration of the hydrochloric acid is also low, presumably pure cyanacetic ester may be obtained, but such conditions are neither the best nor the most convenient. Sulphuric acid may, however, be used and pure cyanacetic ester obtained, and that in theoretical amount if proper proportions of reagents and proper conditions as to temperature and time of action are employed.

Art. XXIX.—*On the Preparation of Malonic Acid or its Ester from Monochloracetic Acid;* by I. K. Phelps and E. W. Tillotson, Jr.

[Contributions from the Kent Chemical Laboratory of Yale University—clxxxv.]

Kolbe,* starting with chloracetic acid, Müller† and Finkelstein‡, with chloracetic ester, and Franchimont§, with bromacetic ester, have shown that, by acting on the above-named derivatives of acetic acid with potassium cyanide, and subsequently treating with potassium hydroxide, potassium malonate is formed. They give no data showing the yield of malonic acid obtainable under the conditions of experimentation. Von Miller‖ treated potassium chloracetate with potassium cyanide, boiled with potassium hydroxide, saturated with hydrochloric acid, evaporated to dryness, and extracted with ether. From 100 grm. of monochloracetic acid he obtained 75 grm. of malonic acid, or 70 per cent of that theoretically possible. Conrad¶ followed a similar procedure except that instead of evaporating to dryness, he precipitated the calcium malonate. The ester was prepared by saturating a mixture of calcium malonate and absolute alcohol with hydrochloric acid, distilling off the alcohol, washing the ester with a solution of sodium carbonate, and drying over calcium chloride. A yield of 63 per cent of that theoretically possible from the amount of chloracetic acid used was obtained by this method. Grimaux and Tcherneak** and later Bourgoin,†† after acting on sodium or potassium chloracetate with potassium cyanide, saturated the water solution with gaseous hydrochloric acid, evaporated to dryness and extracted the malonic acid with ether. The earlier paper reports a yield of 34 per cent, the later one of 64 per cent of the theoretical amount of malonic acid. Claisen and Venable‡‡ evaporated the aqueous solution of potassium cyanacetate, first obtained, until the temperature reached 135°, pulverized the mass, added alcohol and saturated the mixture with gaseous hydrochloric acid. The product was poured into water, extracted with ether, and the ethereal solution dried over calcium chloride. By this procedure 55 per cent of the theoretical amount of malonic ester was obtained. Noyes§§ treated the pulverized mass of salt, obtained as described above, with a mixture of equal parts of alcohol and sulphuric acid and boiled under a return condenser, added a solution of sodium

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* Ann., cxxxi, 348.

† Ann., cxxxi, 350.

‡ Ann., cxxxiii, 338.

§ Berichte, vii, 217.

‖ Jour. prakt. Chem. [2], xix, 326.

¶ Ann., cciv, 121.

** Bull. Soc. Chim., xxxi, 338.

†† Ibid., xxxiii, 572.

‡‡ Ann., ccxviii, 131.

§§ Jour. Am. Chem. Soc., xviii, 1105.

No.	Chloracetic acid grm.	Potassium cyanide grm.	Temperature of reaction	Malonic ester Theory grm.	Malonic ester Found grm.	Malonic ester Per cent
			A			
(1)	200	175	110°	338·8	264·77	78·2
(2)	200	165	110°	338·8	295·73	87·3
(3)	200	165	90°–95°	338·8	293·14	86·5
(4)	200	165	90°–95°	338·8	285·24	84·2
(5)	200	165	90°–95°	338·8	295·26	87·1
			B			
(1)	200	165	90°–95°	338·8	295·76	87·3
(2)	200	165	90°–95°	338·8	297·49	87·8
			C			
(1)	200	165	110°	338·8	296·24	87·4
(2)	200	165	90°–95°	338·8	292·65	86·3

carbonate and extracted the malonic ester with ether. The ether was distilled off, and the ester fractioned under diminished pressure. By recovering and esterifying the acid ester from the sodium carbonate solution, he obtained a weight of malonic ester equal to that of the chloracetic acid employed, or about 60 per cent of that theoretically possible.

In an earlier paper* in this Journal, the best conditions for the esterification of malonic acid were studied. In a later paper† a study of the conversion of cyanacetic ester to malonic ester was reported. In preparing material for use in those papers the synthesis from chloracetic acid was employed. It seemed worth while to study these syntheses further and apply the results of the two earlier papers to the practical preparation of malonic ester. This paper reports the results of such a study.

For the work described in this paper, impure commercial monochloracetic acid was twice fractionally distilled at atmospheric pressure, using portions boiling within limits of one to one and one-half degrees. The acid obtained in this manner was found to be about 95 per cent pure as shown by the following analyses, made according to Carius:

I. 0·1808 grm. of acid gave 0·2608 grm. of silver chloride.
Cl=35·64 per cent.
II. 0·0939 grm. of acid gave 0·1347 grm. of silver chloride.
Cl=35·47 per cent.
Calculated for $C_2H_3O_2Cl$, Cl=37·53 per cent.

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* This Journal, xxvi, 143.

† Ibid, xxvi, 257.

Potassium cyanide of 96–98 per cent purity was used for the experiments in series A of the table. For those of series B, pure commercial cyanide containing ammonia, and for those of series C, pure commercial potassium cyanide free from ammonia and cyanate was employed. An analysis of the sample used in the experiments in series C gave the following results.

I. 0·2372 grm. of potassium cyanide gave ·4579 grm. of silver cyanide. CN=37·50 per cent.
II. 0·2682 grm. of potassium cyanide gave ·5198 grm. of silver cyanide. CN=37·65 per cent.
Calculated for KCN, CN=39·95 per cent.

The alcohol made use of in the conversion to malonic ester and that employed in the process of esterification was alcohol of commerce, made as free from water as possible by repeated distillations over calcium oxide.

In all the experiments in the table, except those specially treated, 200 grm. of monochloracetic acid, contained in a liter flask, was treated with about 300 grm. of pure hydrous sodium carbonate of commerce, and 50^{cm^3} of water added to start the reaction. Good results were obtained, in experiments not recorded, using the anhydrous sodium carbonate dissolved in 250^{cm^3} of water. The advantage in the use of the hydrous salt lies in the fact that the solution of sodium chloracetate is kept cold during the process of neutralization, thus keeping the hydrolysis of the chloracetate at a minimum. In fact, under the above conditions, a temperature low enough to freeze the mass is nearly always obtained. It is usually convenient to hurry the reaction by standing the flask in water at room temperature. In experiment (1) of series B, potassium carbonate was used instead of sodium carbonate, but there appeared to be no advantage in its use, since the potassium sulphate formed on acidifying with sulphuric acid was not less soluble than sodium sulphate under the conditions of experimentation. When the chloracetic acid was entirely neutralized, the solution was poured into a solution of 165 grm. of potassium cyanide in 250^{cm^3} of water heated to 70–80°, and after the vigorous action had taken place, the solution was boiled for about five minutes to complete the reaction. The solution was then cooled and acidified with sulphuric acid, using the action of a drop of the liquid with logwood paper as a test of acidity. About 100^{cm^3} of concentrated sulphuric acid were required for each experiment. After cooling the precipitated salt was filtered off and the water solution evaporated to dryness. In experiment (1) of series A, this was done at the temperature of the steam bath. In the remaining experiments of the table, it was accomplished under diminished pressure by heating the flask in a water bath at 70–80°, collecting the distillate in a side-necked receiver which was kept cool by a stream of water flowing over it continuously. The salt which had been filtered off from the water solution was shaken up in a flask with 200^{cm^3} of 95 per cent alcohol, filtered, and the salt washed on the filter with 100^{cm^3} of alcohol of the same strength. These alcoholic solutions were then added to the residue, obtained by evaporation of the water solution, warmed in a water bath and shaken till homogeneous. The insoluble salt was filtered off, shaken up again with $100–200^{cm^3}$ of hot 95 per cent alcohol, and again filtered. The combined alcoholic solutions contained in a liter flask were then freed from alcohol, water, and low-boiling products by heating under diminished pressure with a water bath at 60°, collecting the distillate as before. The residue, consisting chiefly of cyanacetic acid, cyanacetic ester, and some sodium or potassium salt, was treated by the method described in a former paper* for the conversion of cyanacetic ester to malonic ester. For these experiments, 600^{cm^3} of absolute alcohol with 5^{cm^3} of sulphuric acid, sp. gr. 1·84, were placed with the product obtained as described above, in a two liter flask fitted with a reflux condenser and kept cool in a mixture of ice and salt, and the solution saturated with gaseous hydrochloric acid, dried by bubbling through concentrated sulphuric acid. At the end of about twelve hours saturation was usually complete. The ice mixture was then replaced by a water bath and the solution boiled under the return condenser for two hours, passing the current of hydrochloric acid through the mixture continuously. The precipitated ammonium salt was then filtered off, shaken up with 100^{cm^3} of absolute alcohol, filtered again and washed with absolute alcohol. The alcoholic solutions were then collected in a liter flask fitted for esterification, as described in a former paper† from this laboratory, and 700^{cm^3} of absolute alcohol distilled during a period of three to four hours through the solution of ester, which was kept at a temperature of 100–110°. The resulting product was purified by treating with ice and a solution of sodium carbonate and shaking out with ether. The ether and all low-boiling products were then removed and the pure malonic ester distilled under diminished pressure, as described in the paper to which reference has been made. The ester obtained in this manner boiled within reasonable limits and was nearly pure ethyl malonate. Further evidence of its purity is furnished by the fact that, on

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* This Journal, xxvi, 143.

† This Journal, xxiv, 194.

hydrolysis of the fractionated material, pure* malonic acid was obtained.

In experiments (3), (4) and (5) in series A, (1) and (2) in series B, and (2) in series C of the table, the reaction between the sodium chloracetate and potassium cyanide was made to take place at a temperature of 90°–95°, by allowing the cold solution of chloracetate to run slowly from a separatory funnel into the hot cyanide solution, an operation which took from fifteen to twenty minutes. In the other experiments the two solutions were mixed and the reaction allowed to take place vigorously, the temperature under these conditions reaching 110°. It was noticed in this reaction that if the chloracetate solution was distinctly alkaline a nearly colorless solution resulted, while if acid considerable color developed. The amount of color seemed to increase with the length of time of the reaction. Thus when the solutions were mixed and a vigorous action took place, less color resulted than when the reaction went at 90°–95° for fifteen minutes, but even then the coloration was small in comparison to that formed in experiments not recorded in the table, in which the reaction was made to take place at the temperature of ice water during a period of twelve hours. The color is possibly due to dark-colored polymeric products formed from hydrocyanic acid. Hence it is advantageous to allow the reaction between potassium cyanide and sodium chloracetate to proceed in alkaline solution at a temperature of about 100°. But these conditions are favorable for the conversion of the cyanacetate to a malonate, which is to some extent decomposed in the hot alkaline solution as shown by Van't Hoff,† who explained the decomposition as taking place according to the following equation: $CH_2(COOK)_2 + KOH = CH_3COOK + K_2CO_3$. For this reason prolonged boiling after the reaction is over is not desirable. On acidifying, the slight excess of sulphuric acid produces a small amount of hydrochloric acid, which, in the process of evaporation of the aqueous solution of cyanacetic acid, may also cause the formation and decomposition of some malonic acid. This is shown in experiment (1) of series A, in which the acid solution was evaporated on a steam bath. When the volume of liquid became small, decomposition was apparent, through the escape of bubbles of carbon dioxide. This decomposition was minimized in all the remaining experiments, except experiment (4) of series A, by evaporating at a lower temperature, under diminished pressure. In order, if possible, to entirely prevent this decomposition through the hydrolyzing effect of the strong acid, the excess of sulphuric acid was removed, in

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* This Journal, Phelps and Weed, xxvi, 138.

† Berichte, vii, 1382.

the case of experiment (4) of series A, by adding a solution of sodium acetate in excess, testing the disappearance of acidity of the solution with logwood paper. The slightly lower yield would indicate that sodium cyanacetate had been formed from the sodium acetate and the free cyanacetic acid present.

Some loss always occurred during the distillation of the alcohol from the alcoholic solution of cyanacetic acid. The alcoholic distillates, averaging 500^{cm^3}, from five experiments not recorded in the table but made by the procedure described, were separately distilled through a Hempel column to small volume and the remainder heated at 60°, under diminished pressure, till the manometer registered 15^{mm}. The weighed residues were combined and esterified. From the weight of cyanacetic ester so obtained it was found that when 500^{cm^3} of alcohol, containing some water, were distilled at 60° under diminished pressure, from a solution containing about 180 grm. of cyanacetic acid, there also distilled 7·1 grm. of cyanacetic ester, which is equivalent to 10 grm. of malonic ester, or three per cent for each experiment. It has been shown in a former paper* that the loss of malonic ester, inherent in the process employed for the conversion of cyanacetic ester to malonic ester, was about three grams for seventy grams of malonic ester, or 4·3 per cent. If these constant losses be considered, it is evident that the results shown in the table are approximately 7·3 per cent lower than the amount of malonic ester which would have been obtained had there been no loss during the process.

From the experiments in series A, in which potassium cyanide of 96–98 per cent purity was used in excess, the results are as good as those in series B, in which pure cyanide of commerce containing ammonia was employed, and even as good as those in series C, in which cyanide free from ammonia and cyanate was made use of, other conditions being the same. Thus it would seem that if the potassium cyanide is in excess, impurities in the cyanide to the extent of three or four per cent do not materially affect the reaction with sodium chloracetate.

In experiment (2) of series C there was much evolution of carbon dioxide when sodium carbonate was added in the process of recovery of the pure ester. This was presumably due to the excess of sulphuric acid which was added previously to liberate the cyanacetic acid. Too large an excess is not desirable, as it retards esterification, either by holding back water or by forming water and ethyl ether in reacting with alcohol at the temperature 100°–110°, at which esterification took place. The slight variations in yield among otherwise similar experiments may be due to variations in the excess of sulphuric acid present.

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* This Journal, xxvi, 260.

From the work recorded here it is evident that the reaction between potassium cyanide and sodium chloracetate to form sodium cyanacetate proceeds best in alkaline solution. This reaction may take place vigorously at 110° or slowly at 90°–95° without materially affecting the yield of malonic ester. For the best results the alkaline solution of sodium cyanacetate should not be evaporated to dryness at a high temperature or even boiled for a long time, since these conditions are favorable for the formation and decomposition of the sodium malonate formed. The aqueous solution of cyanacetic acid is best evaporated to dryness under diminished pressure at a temperature of 70°–80°, and the alcoholic solution at about 60°. In removing the alcohol under diminished pressure there is a constant loss equivalent to three per cent of malonic ester, and in the process employed for converting the cyanacetic ester to malonic ester and recovering the latter in pure form, there is an additional loss of 4·3 per cent. If these losses be considered we have, in the case of the several higher results shown in the table, from 94·3 to 95·1 per cent of the theoretical amount of malonic ester accounted for. Further, if we take into account that the chloracetic acid employed was but 95 per cent pure, as shown by analysis, it seems that the results given are from 99·3–100 per cent of the theoretical amount for the chlorine content of the chloracetic acid used. That is to say, potassium cyanide and sodium chloracetate, in alkaline solution at about 100°, react to give a theoretical amount of sodium cyanacetate and potassium chloride. Or, again, the theory for malonic ester obtained from 200 grm. of monochloracetic acid of 95 per cent purity is 321·8 grm. and the yields actually obtained, leaving out of account experiments (1) and (4) of series A, average 295·18 grm. or 91·7 per cent instead of 87·1 per cent in the table, in which the theory is calculated on the basis of pure monochloracetic acid.

Thus malonic ester in large quantities may be made in nearly theoretical amount from monochloracetic acid if the procedure as outlined above be followed. The essential points are, an excess of potassium cyanide, reacting in alkaline solution; the addition of sulphuric acid to the solution of sodium cyanacetate in only slight excess; the evaporation of the aqueous and alcoholic solutions of cyanacetic acid at low temperature, which is most readily done under diminished pressure; the conversion to malonic ester and the purification of the same by the procedure described above. Under these conditions, if the chloracetic acid be only 95 per cent pure, about 87 per cent of the theoretical amount of malonic ester may be obtained, or figuring it on the chlorine content of the chloracetic acid, about 92 per cent, which is an improvement of about thirty per cent on the best previous methods known to us.

Pure malonic acid was obtained from ester, prepared in this way, for use in an earlier paper* on the esterification of malonic acid. The ester was fractionally distilled under atmospheric pressure with a Hempel column. Portions boiling within two tenths of a degree were converted into malonic acid by heating equal parts of malonic ester and water with a few drops of nitric acid at a temperature of about 60° for some time after the mixture had become homogeneous. The solution was then evaporated in an open dish at a temperature of about 50° to the point of saturation, and the malonic acid which separated on cooling was recrystallized from hot water. In this manner pure malonic acid may be obtained with only slight loss of material.

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* This Journal, xxvi, 243.

Art. XXX.—*On the Preparation of Cyanacetic Acid and its Ester from Monochloracetic Acid;* by I. K. Phelps and E. W. Tillotson, Jr.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxxiii.]

Kolbe,[*] in synthetizing malonic acid, states that if the solution obtained by acting on chloracetic acid with potassium cyanide be acidified with sulphuric acid and extracted with ether, cyanacetic acid is obtained, which on boiling with potassium hydroxide is converted to potassium malonate. Müller[†] obtained cyanacetic ester "boiling above 200°" by treating chloracetic ester in alcoholic solution with potassium cyanide. Finkelstein[‡] used chloracetic ester and an aqueous solution of potassium cyanide, boiling till all the ester had gone into solution, evaporating to dryness, acidifying the residue with hydrochloric acid and extracting with ether. On evaporation of the ether cyanacetic acid was obtained. Meeves[§] also acted on chloracetic ester with potassium cyanide in a water solution, evaporated, acidified with sulphuric acid, and extracted with ether. The acid obtained on evaporation of the ether was purified by treating with lead carbonate, filtering off the excess of carbonate and insoluble lead malonate and decomposing the solution of lead cyanacetate with hydrogen sulphide; but as in the case of the other investigators mentioned above, no results were given by him showing the amount of cyanacetic acid obtainable from a given weight of chloracetic acid. Grimaux and Tcherneak[‖] caused sodium chloracetate and potassium cyanide to react, extracted the cyanacetic acid with ether according to Meeves' procedure and obtained about 75 per cent of the theoretical amount of cyanacetic acid. Van't Hoff[¶] states that he obtained a nearly theoretical yield from chloracetic acid, but gave no definite information as to how it was obtained. Fiquet[**] followed in general the same procedure as Grimaux and Tcherneak, acidifying with hydrochloric acid instead of sulphuric acid, and obtained 70 per cent of that theoretically possible. Noyes,[††] after boiling chloracetic ester and potassium cyanide with methyl alcohol, obtained 50 per cent of the theoretical yield of cyanacetic ester, boiling within limits of ten degrees.

In a former paper[‡‡] it has been shown from the amount of malonic ester obtained that sodium chloracetate and potassium

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[*] Ann., cxxxi, 348.

[†] Ann., cxxxi, 350.

[‡] Ann., cxxxiii, 338.

[§] Ann., cxliii, 201.

[‖] Bull. Soc. Chim., xxxi, 338.

[¶] Berichte, vii, 1382.

[**] Jour. Am. Chem. Soc., xxvi, 1545.

[††] Ann. Chim. [6], xxix, 439.

[‡‡] This Journal, xxvi, 267.

				Cyanacetic ester		
No.	Chloracetic acid grm.	Potassium cyanide grm.	Temperature of reaction	Theory grm.	Found grm.	Per cent.
			A			
(1)	200	165	90°–95°	239·4	219·78	91·4
(2)	200	165	110°	239·4	224·15	93·6
(3)	200	165	110°	239·4	222·00	92·7
(4)	200	165	110°	239·4	220·00	91·9
			B			
(1)	200	165	0°–5°	239·4	213·30	89·1
(2)	200	165	90°–95°	239·4	218·72	91·4
(3)	200	165	90°–95°	239·4	220·04	91·9
(4)	200	165	110°	239·4	207·68	86·8
(5)	200	165	110°	239·4	206·63	85·1

cyanide react in alkaline solution at 100° to form the theoretical amount of sodium cyanacetate. The work recorded in this paper is a study of the formation of ethyl cyanacetate from monochloracetic acid, making use of the best conditions for the esterification of cyanacetic acid as described in an earlier paper* in this Journal.

For the work described in this paper the impure monochloracetic acid of commerce was fractionally distilled twice at atmospheric pressure, using portions boiling within limits of one and one-half degrees. The acid so obtained was found, by analysis given in a former paper,† to be about 95 per cent pure. Commercial potassium cyanide of 96–98 per cent purity was used in all the experiments. The alcohol employed in esterification of the cyanacetic acid was made as free as possible from water by repeated distillations from calcium oxide.

In all the experiments except those in which the treatment was special, 200 grm. of monochloracetic acid of the purity described above, was treated in a liter flask with about 300 grm. of hydrous sodium carbonate and 50$^{cm^3}$ of water to start the reaction. The temperature of the mass usually became so low that the mixture was frozen. The action may be hastened by immersing the flask in water at room temperature. Good results were also obtained by using about 110 grm. of anhydrous sodium carbonate and 250$^{cm^3}$ of water, but since the reaction with the hydrous carbonate takes place with cooling, there is less tendency towards hydrolysis of the chloracetate. The alkaline solution of sodium chloracetate was then poured into a hot solution of 165 grm. of potassium cyanide in 250$^{cm^3}$ of water and after the action had taken place the solution was boiled for five minutes to complete the reaction. To the cooled solution was then added sulphuric acid in slight excess,

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* This Journal, xxvi, 264.

† This Journal, xxvi, 268.

using a drop of the solution with logwood paper as a test of acidity. The precipitated salt was then filtered off and the water distilled from the cyanacetic acid and other non-volatile material under diminished pressure by heating the flask in a water bath at 70°–80° and collecting the distillate in a side-necked flask as a receiver, which was kept cool by allowing a stream of water to flow over it continuously. The salt which remained on the filter was washed with 300^{cm^3} of 96 per cent alcohol, and the alcoholic solution added to the cyanacetic acid residue remaining after the aqueous solution had been distilled under diminished pressure. The mixture was well shaken, filtered, and the salt shaken up with 100^{cm^3} of alcohol of 96 per cent strength, filtered and washed with alcohol. The combined alcoholic solutions were then evaporated under diminished pressure, heating the flask in a water bath at 50°–60° and collecting the distillate as before, continuing distillation till the manometer showed 15^{mm} pressure, to insure removal of all the water. To the residue, which consisted chiefly of cyanacetic acid and its ester, was added 100^{cm^3} of absolute alcohol and 5^{cm^3} of sulphuric acid, sp. gr. 1·84. Then the mass was esterified at 100°–110° for 2·5 to 3 hours with 500^{cm^3} of absolute alcohol, using the special arrangement of flasks for esterification described in a former paper* from this laboratory. The crude product was then purified by treating with ice and a solution of sodium carbonate and shaking out with ether. The ethereal solution was then freed from low-boiling products and distilled under diminished pressure in the usual manner.

In experiment (1) of series B, the potassium cyanide and sodium chloracetate were made to react in the cold, the flask standing in ice water for twelve hours. In experiments (1) of series A, and (2) and (3) of series B, the cold alkaline solution of chloracetate, contained in a separating funnel, was slowly run into the hot solution of potassium cyanide. The time employed was fifteen to twenty minutes and the temperature was kept at 90°–95° by the heat of the reaction. In the other experiments of the table the two solutions were mixed immediately and the action allowed to take place vigorously, the temperature being usually about 110°. It has been shown in the former paper to which reference has been made, that this reaction proceeds more smoothly in an alkaline solution at a temperature of about 110°, but these conditions are unfavorable for the production of pure cyanacetic acid or ester, since cyanacetates are converted to malonates in hot alkaline solution. For this reason prolonged boiling after the reaction is over is not desirable. On acidifying, the slight excess of sulphuric

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* This Journal, xxiv, 194.

acid acting on the chlorides present produces a small amount of hydrochloric acid, which, in the process of evaporation, also tends to the formation of malonic acid. In series A there was a slight excess of sulphuric acid in each experiment. The ester obtained, after fractioning under diminished pressure, appeared to contain malonic ester as shown by the following analyses:

I. 0·5060 grm. of ester gave 51·5$^{cm^3}$ of moist nitrogen at 21° and 762·6^{mm}. N = 11·39 per cent.
II. 0·5070 grm. of ester gave 51·2$^{cm^3}$ of moist nitrogen at 22° and 765·2^{mm}. N = 11·52 per cent.
Calculated for $C_5H_7O_2N$, N = 12·40 per cent.

In the experiments of series B, after adding a slight excess of sulphuric acid, as indicated by logwood paper, enough of a saturated solution of sodium acetate was added to destroy the excess of sulphuric acid, logwood paper again being the indicator. The ester obtained in this manner, after being fractioned under diminished pressure, gave the following analyses:

I. 0·5020 grm. of ester gave 55·2$^{cm^3}$ of moist nitrogen at 23° and 762·3^{mm}. N = 12·47 per cent.
II. 0·5004 grm. of ester gave 55·0$^{cm^3}$ of moist nitrogen at 20° and 758·2^{mm}. N = 12·54 per cent.
Calculated for $C_5H_7O_2N$, N = 12·40 per cent.

It is plain therefore that if pure cyanacetic ester is to be obtained, the water solution of cyanacetic acid must not be evaporated in the presence of mineral acids, but in the presence of acetic acid no considerable decomposition takes place. The operation is most conveniently performed under diminished pressure, since the low temperature necessary to remove the water under diminished pressure is unfavorable for the formation of malonic acid.

Some loss always occurred during the distillation of the alcoholic solution of cyanacetic acid. This loss has been shown in the former paper,* on the preparation of malonic ester, to be 7·1 grm. of cyanacetic ester or about three per cent. It has also been shown in a former paper,† that the loss inherent in the process used for recovery of pure ester from the crude product obtained in the esterification flask was 1·67 grm. for 70 grm. of pure ester or 2·4 per cent. Assuming that this percentage error holds for large amounts, we have approximately 5·4 per cent of cyanacetic ester lost during the procedure.

In an earlier paper‡ it was shown from the yield of malonic ester obtained that if the purity of the chloracetic acid used and the loss of malonic ester inherent in the process be taken into

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* This Journal, xxvi, 272.

† This Journal, xxvi, 265.

‡ This Journal, xxvi, 273.

account, the reaction between sodium chloracetate and potassium cyanide was practically quantitative. It is therefore possible to calculate from the amount of malonic ester obtained from the chloracetic acid used, the amount of cyanacetic ester which might be expected from 200 grm. of the same quality of chloracetic acid. A series of seven experiments similarly carried out gave an average of 87·1 per cent of malonic ester, with a loss inherent in the process of converting the cyanacetic to the malonic ester of 4·2 per cent. This gives 309·32 grm. of malonic ester, which is equivalent to 218·57 grm. of cyanacetic ester from 200 grm. of chloracetic acid. The loss sustained by the process employed for the recovery of the ester from the crude product obtained in the esterification flask, has been shown in a former paper* to be 1·67 grm. for 70 grm. of cyanacetic ester, and is presumably 5 grams for the 218·57 grm. under consideration in these experiments. Thus if the ester formed is pure ethyl cyanacetate, we should not expect to obtain more than 213·57 grm., and higher yields may be explained by the conversion of some of the cyanacetic ester into malonic ester. This explanation is supported by the analyses, given above, of the ester obtained in experiment (2) of series A, and appears justified since in the experiments of series A there was an excess of sulphuric acid while the aqueous solutions of cyanacetic acid were being evaporated to dryness. The higher yields obtained in experiments (2) and (3) of series B are ascribed to the formation of sodium malonate from sodium cyanacetate in the hot alkaline solution. In these experiments the reaction took place slowly for a period of fifteen to twenty minutes, which allowed more hydrolysis to take place than in experiments (4) and (5) of series B, in which the action was over in five minutes or less. The lower results in experiments (4) and (5) of series B are explained on the assumption that the cyanacetic acid, reacting with the excess of sodium acetate, forms an equilibrium mixture and, since the sodium cyanacetate is not dissolved by the alcohol, a loss occurs.

The results of the work here described are in agreement with those of a former paper, which show that potassium cyanide and sodium chloracetate react quantitatively in alkaline solution at 110°. They also show that cyanacetic ester of high purity may be prepared in large amounts, and in good yield, from monochloracetic acid if precautions be taken to minimize the transformation to malonic acid. To this end the reaction between sodium chloracetate and potassium cyanide should take place quickly, the alkaline solution of sodium cyanacetate should not be boiled for a long time, and the solution of cyanacetic acid, containing an excess of mineral acid, must not be evaporated

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* This Journal, xxvi, 264.

to dryness at a high temperature. However, it may be quickly and conveniently evaporated by heating with a water bath at 70°–80° under diminished pressure, in which case the cyanacetic ester formed is of 90–95 per cent purity. Experiments (2), (3) and (4) of series A were performed under such conditions. If pure cyanacetic ester is to be obtained, the excess of mineral acid must be removed by adding sodium acetate. In this case the yield is not so good, but the ester, after fractioning under diminished pressure, is pure ethyl cyanacetate. This procedure was followed in experiments (4) and (5) of series B.

Pure cyanacetic acid was obtained from the ester prepared in this way for use in an earlier paper* on the esterification of cyanacetic acid. Two parts of water with one of ester and a few drops of nitric acid were heated at a temperature of about 60° for some time after the mixture had become homogeneous. The solution was then evaporated in an open dish, at a temperature of 50°–60°, to the point of saturation. The cyanacetic acid which separated on cooling was recrystallized from a mixture of ether and chloroform. In this manner pure cyanacetic acid, melting at 66·1°–66·4° (corrected), was obtained in quantity and in good yield.

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* This Journal, xxvi, 264.

ART. XXXI.—*Researches on the Influence of Catalytic Agents in Ester Formation. Hydrobromic Acid and Zinc Bromide in the Formation of Ethyl Benzoate*; by I. K. and M. A. PHELPS and E. A. EDDY.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxxvii.]

GOLDSCHMIDT* has measured the rate of esterification of benzoic acid with ethyl alcohol, using hydrochloric and hydrobromic acids as catalyzers. The results in the use of these two catalytic agents for a temperature of 25° are so nearly the same that he concludes that hydrochloric and hydrobromic acids under the conditions of his experiments have the same efficiency as catalytic agents in ester formation. Goldschmidt† and many others, from similar physico-chemical measurements given in recent literature, have concluded that the efficiency of a given catalyzer depends upon the concentration of the catalyzer and upon the degree of dissociation of the catalyzer in alcoholic solution.

The amount of ester formed from benzoic acid in presence of sulphuric acid, or hydrochloric acid, or hydrochloric acid and zinc chloride as catalyzers, with different amounts of ethyl alcohol acting for different lengths of time, has been shown in a former paper‡ in this Journal. The esterification of the benzoic acid was made in flasks specially arranged as illustrated in an earlier paper§ in this Journal, where the action of zinc chloride and hydrochloric acid, as catalyzers, was shown in the formation of ethyl succinate. The results given in the paper concerning the esterification of benzoic acid show that under the conditions of the experiments made, increasing the concentration of the catalyzers up to a certain limit increases the amount of ester produced with a given amount of alcohol acting in a given time on a given amount of benzoic acid. Further increase in the amount of catalyzers beyond this limiting concentration caused a decided falling off in the amount of ester produced. And, finally, the results referred to show that the yields of ester produced bear no relationship to the degree of ionization of the catalyzer. For example, hydrochloric acid dissociates to a greater extent than sulphuric acid, but with hydrochloric acid as a catalytic agent yields beyond 90·4 per cent were not obtained even when a mass of 50 grm. of benzoic acid was treated with 400^{cm^3} of alcohol containing 25 per cent of hydrochloric acid during eight and a half hours, interpolating a fractionation under diminished pressure to remove low-boiling products, especially whatever water formed during

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* Berichte, xxviii, 3218.

† Ibid., xxxix, 711.

‡ This Journal, xxv, 39.

§ This Journal, xxiv, 194.

esterification that had not been removed under the conditions of the experiment, when half of the alcoholic mixture had acted upon the acid. It is, however, a striking fact that two grams of sulphuric acid with half the amount of alcohol acting about one-third of the same time with the same amount of benzoic acid gives theoretical yields of ester.

In the work recorded here the catalytic action of zinc bromide and hydrobromic acid at different temperatures on benzoic acid with ethyl alcohol is brought into comparison with the similar action of zinc chloride and hydrochloric acid recorded in the paper to which reference has been made, as well as in this paper.

For this work ethyl alcohol was prepared as free from water as possible by repeated distillations with calcium oxide. The benzoic acid used was the pure benzoic acid of commerce. For the preparation of pure, dry hydrobromic acid the pure bromine of commerce was freed from chlorine by long standing, with frequent shaking, in contact with an aqueous solution of potassium bromide,* before distilling off the bromine. The hydrobromic acid gas was prepared by allowing the purified bromine to act on a mixture of red phosphorus and water, the gas set free being purified by passing first through layers of moist red phosphorus and glass wool contained in one leg of a U-tube, the outer leg of which, to dry the gas completely, contained layers of phosphorus pentoxide and glass wool. The hydrobromic acid thus prepared was dissolved in chilled alcohol in the concentrations given in the tables. These concentrations were chosen of such values that the hydrobromic acid in these experiments was in molecular proportion to the hydrochloric acid in the experiments to which reference has been made. Pure zinc bromine was prepared for use in two different ways. The pure zinc bromide of commerce was fused in an atmosphere of pure hydrobromic acid before granulating the melted zinc bromide. Zinc bromide was also prepared by heating in a flask connected to a return condenser the pure zinc of commerce at a temperature above the melting point of zinc with bromide purified, as described above, for the preparation of hydrobromic acid, and then dried with sulphuric acid before distilling. The pure zinc bromide made in this way was melted, as in the case of the commercial sample, in an atmosphere of dry hydrobromic acid, heated to expel any excess of hydrobromic acid, and then granulated. The amounts of zinc bromide used corresponded molecularly to the zinc chloride used in the esterification of benzoic acid in the work to which reference has been made.

In all the experiments given in this paper the procedure was

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* Richards and Wells, Proc. Amer. Acad., xli, 440.

similar to that given in the former paper in this Journal on the esterification of benzoic acid to which reference has been made. In brief the treatment consisted in heating at a definite temperature a given weight of benzoic acid in the presence of a small amount of alcohol with a certain amount of hydrobromic or hydrochloric acid, or with an alcoholic solution of hydrobromic or hydrochloric acid, and zinc bromide or chloride in definite amount. Into this mixture a known amount of alcohol and hydrobromic or hydrochloric acid in definite amount was driven at a uniform rate in vapor condition. The vapor issuing from the flask in which the esterification took place was fractioned by passing through a Hempel column attached to an ordinary condenser. It has been shown in the earlier paper that benzoic ester is retained completely in the flask in which the benzoic acid is esterified. The ester was isolated in pure condition by shaking out the mixture of the crude product with ether, treating with sodium carbonate, and distilling under diminished pressure in the manner described in the earlier work on benzoic ester.

It appears from an inspection of the results recorded in Table I that hydrobromic acid as a catalyzer varies in its efficiency according to its concentration, and according to the temperature at which esterification takes place. This is seen in comparing experiments (1) with (10) and (1) with (5), or (10) with (12) and (13). It is also clear that in comparing (8) with (9) that the rate of flow of a given amount of alcoholic mixture is of influence. A certain amount flowing rapidly is able to esterify 10 per cent less benzoic acid than half that amount of alcohol even in shorter time, as is seen by comparing (4) with

TABLE I.

No.	Benzoic acid grm.	Alcohol with HBr		Temperature	Time of action		Benzoic ester		
		cm³	per ct.		hrs.	min.	Theory grm.	Found grm.	per ct.
(1)	50	200	2·77	85°– 90°	2	10	61·48	41·18	66 98
(2)	50	200	2·77	90°	1	55	61·48	39·45	64·17
(3)	50	200	2·77	100°	2	35	61·48	29·30	47·66
(4)	50	200	2·77	100°–110°	1	45	61·48	27·00	43·92
(5)	50	200	2·77	100°–120°	3	15	61·48	26·40	42·94
(6)	50	200	2·77	125°–130°	1	55	61·48	17·70	28·79
(7)	50	200	2·77	125°–140°	2	5	61·48	15·58	25·34
(8)	50	400	2·77	100°	2	5	61·48	20·31	33·03
(9)	50	400	2·77	100°	4	25	61·48	35·96	58·49
(10)	50	200	27·74	85°– 90°	3	..	61·48	56·05	91·17
(11)	50	200	27·74	90°–100°	3	50	61·48	50·96	82·89
(12)	50	200	27·74	90°–100°	3	..	61·48	51·75	84·17
(13)	50	200	27·74	100°	3	..	61·48	41·05	66·77

(8). In comparing (8) and (9), lengthening the time of action of the alcoholic mixtures, other conditions remaining the same, increases the amount of ethyl benzoate formed.

In the results in Table (II), where zinc bromide is used as catalyzer with the hydrobromic acid, no difference was found in the amount of benzoic acid esterified by the two samples of zinc bromide. It is seen from a comparison of experiments (6) with (10) and (12) with (20) that under definite conditions the greater the concentration of hydrobromic acid with a given amount of zinc bromide present, the greater the amount of benzoic acid esterified. When these experiments are compared with (1) and (11) of Table I it at once becomes evident that zinc bromide as well as hydrobromic acid has here a catalytic effect. The greater the amount of either catalyzer present the greater the yield under conditions otherwise closely similar, as is seen in comparing (4), (14) and (24) together, also (2) with (12). The largest amounts of zinc bromide used seem to retard esterification, as appears when (2) and (12) are com-

TABLE II.

No.	Benzoic acid	$ZnBr_2$	Alcohol with HBr		Temperature	Time of action		Benzoic ester		
	grm.	grm.	cm³	per ct.		hrs.	min.	Theory grm.	Found grm.	per ct.
(1)	50	1·7	200	2·77	90°–100°	1	35	61·48	34·78	56·57
(2)	50	1·7	200	2·77	90°	1	50	61·48	36·34	59·19
(3)	50	1·7	200	2·77	100°–150°	2	10	61·48	25·12	40·92
(4)	50	1·7	200	2·77	125°–150°	2	15	61·48	26·15	42·53
(5)	50	1·7	200	2·77	100°	2	25	61·48	42·45	69·04
(6)	50	1·7	200	2·77	90°	3	30	61·48	44·06	71·67
(7)	50	1·7	300	2·77	100°	3	5	61·48	49·76	80·93
(8)	50	1·7	300	2·77	100°–110°	3	50	61·48	45·05	73·11
(9)	50	1·7	400	2·77	100°	2	5	61·48	48·75	79·29
(10)	50	1·7	200	27·74	85°– 90°	3	..	61·48	55·28	89·91
(11)	50	17·	200	2·77	100°	1	30	61·48	46·36	75·40
(12)	50	17·	200	2·77	100°	2	10	61·48	47·46	77·19
(13)	40	17·	300	2·77	90°–100°	4	..	61·48	57·06	92·81
(14)	50	17·	400	2·77	125°–130°	1	50	61·48	41·46	67·44
(15)	50	17·	400	2·77	125°–135°	2	30	61·48	41·05	66·77
(16)	50	17·	400	2·77	100°	2	35	61·48	57·05	92·79
(17)	50	17·	400	2·77	100°	4	10	61·48	59·74	97·17
(18)	50	17·	400	2·77	125°–130°	4	45	61·48	45·10	73·36
(19)	50	17·	200	27·74	90°–100°	1	50	61·48	59·08	96·09
(20)	50	17·	200	27·74	100°	2	5	61·48	58·36	94·96
(21)	50	17·	200	27·74	85°– 90°	3	..	61·48	58·85	95·72
(22)	50	42·5	200	2·77	85°– 90°	2	15	61·48	31·56	51·34
(23)	50	42·5	200	2·77	100°–110°	2	15	61·48	41·98	68·29
(24)	50	42·5	200	2·77	120°–150°	2	..	61·48	44·05	71·65

pared with (23), but even with the largest amount, as in (23) of Table II, the yield of ester is greater than when no zinc bromide was used under conditions otherwise similar as in (5) and (6) of Table I. The temperature exerts a decided influence here, again, in the presence of different amounts of zinc bromide, as is seen in experiments (2), (3) and (5) when compared with each other, and the same is seen when experiment (15) is compared with (16), also when (17) is compared with (18). The same effect of temperature is not seen when zinc bromide, as second catalyzer, is present in such large amounts as found in experiments (19), (20) and (21) when compared with each other, also in (22), (23) and (24) when they are compared with each other. The rate of flow of the alcohol seems to have a similar influence in presence of the second catalyzer that it had in the presence of hydrobromic acid alone. Experiments (2) and (6) show that, as do also (16) and (17).

In Table III are given results which show the action of hydrochloric acid either alone as catalyzer, or with zinc chloride, as a second catalyzer in esterifying at different temperatures benzoic acid. It is clear from an inspection of results that raising the temperature retards the esterification of benzoic acid by means of hydrochloric acid and zinc chloride, as it does the esterification of benzoic acid by means of hydrobromic acid and zinc bromide. In the work for the former paper the influence of temperatures as high as 125° was studied. No marked effects at this temperature appeared. Attention was called there to the difference in esterification produced by varying the amount of the catalyzer, the amount of alcohol, and the time of action.

TABLE III.

No.	Benzoic acid grm.	$ZnCl_2$ grm.	Alcohol with HCl cm³		Temperature	Time of action hrs.		Benzoic ester Theory grm.		
			cm³	per ct.		hrs.	min.	Theory grm.	Found grm.	per ct.
(1)	50	..	200	1·25	100°–110°	1	40	61·48	37·96	61·74
(2)	50	..	200	1·25	125°–150°	2	20	61·48	24·65	40·09
(3)	50	10	200	1·25	100°–110°	2	10	61·48	58·33	94·88
(4)	50	10	200	1·25	125°–150°	2	..	61·48	50·56	82·24

In all the experiments of Table III, in (4) and (24) of Table II and in (1) of Table I, the alcoholic distillate was collected in four portions and the amount of mineral acid was determined in each portion by titrating the diluted distillates with standardized sodium hydroxide solution in the presence of phenolphthalein as an indicator. The amount of mineral acid left in the flask from which the alcohol, charged with hydrochloric or hydrobromic acid, was distilled, was similarly estimated. The amount of mineral acid left in the esterification flask and neutralized with sodium carbonate in the process of recovery of the crude ester in the experiments (1) and (2) of Table III and (1) of Table I was also estimated. This was done by acidifying the sodium carbonate wash water with nitric acid, the precipitated benzoic acid was filtered off and washed with cold water and the halogen acid in the filtrate was determined gravimetrically as the silver salt. In experiment (1) of Table I the total amount of hydrobromic acid in the residues was found to be 1·34 grm., of which 0·07 grm. was in the alcoholic distillate. In this experiment 4·4 grm. of hydrobromic acid were used, leaving 3·06 grm. of hydrobromic acid, which presumably formed ethyl bromide. In experiment (4) of Table II the amount of hydrobromic acid found in the alcoholic distillate was 0·0102 grm. In experiment (24) of Table II the amount of hydrobromic acid found in the alcoholic distillate was 0·0048 grm. In diluting the first portion of the alcoholic distillate ethyl bromide was found present in such amount as to make the resulting liquid turbid.

These experiments show first that at a temperature 85°–90° about seventy-five per cent of the hydrobromic acid has reacted to form ethyl bromide; second, that the hydrobromic acid which remains as such accumulates in the esterification flask; and, third, that zinc bromide has a catalytic effect upon the action of ethyl alcohol and hydrobromic acid, as might have been anticipated.

Similarly, in experiment (1) of Table III the total residues of hydrochloric acid were found and amounted to 1·84 grm., of which 0·110 grm. were found in the alcoholic distillate and 1·455 grm. in the esterification flask, leaving 0·185 grm. from a total of 2·025 grm. of hydrochloric acid taken with the alcohol, which reacted presumably to form ethyl chloride. In experiment (2) of Table III the total hydrochloric acid found in all residues was 1·485 grm., of which 0·615 grm. was in the alcoholic distillate and 0·595 grm. was in the esterification flask, leaving 0·54 grm. from a total of 2·025 grm. taken in the alcoholic mixture. In experiment (3) of Table III the hydrochloric acid found in the alcoholic distillate was 0·0019 grm., and in (4) of the same table 0·0017 grm. was found in the alcoholic distillate.

The evidence from these experiments proves that, at a temperature of 100°–110°, about ten per cent of the hydrochloric acid present has reacted to form ethyl chloride. At the higher temperature of 125°–150°, a larger amount, about twenty-five per cent, is used in this way. With hydrobromic acid of similar concentration, this sort of action, at the lower temperature of 85°–90°, goes on to a much larger extent. Thus, in experiment (1) of Table I seventy-five per cent of the hydrobromic acid has reacted in this way. Further, the efficiency in ester formation of hydrobromic acid with or without zinc bromide was shown in Tables I and II to be dependent in large measure upon the temperature. The difference in the amount of ethyl chloride formed at the different temperatures, the large amount of ethyl bromide formed under similar conditions of temperature with hydrobromic acid, and the variability in the efficiency of zinc bromide at different temperatures, would indicate that the failure of zinc bromide to act as an efficient catalyzer at higher temperature is due to the almost complete action of hydrobromic acid on alcohol at that temperature to form ethyl bromide and water. The same difference in the effect of temperature is evident with hydrochloric acid, as is shown by experiments (1) and (2) of Table III, but in these cases the action to form ethyl chloride and water makes itself markedly evident only at temperatures that are most unsuited for esterification. And it seems fair to assume that it is this fact that makes hydrochloric acid more advantageous than hydrobromic for use as a catalyzer in esterification.

Presumably it is this difference in catalytic action at different temperatures of hydrobromic acid that explains the difference in the results given by Goldschmidt and those recorded here. Goldschmidt, measuring the rate of esterification at 25°, found hydrochloric and hydrobromic acids equally efficient as catalyzers. In our experiments at higher temperatures they are never equally efficient. In dilute solutions the hydrochloric acid as catalyzer is much more efficient, while with the highest concentrations the hydrobromic acid is more efficient if the esterification is carried on at a temperature of 85°–90°. At 100°–110° the hydrochloric acid is much more efficient, and markedly more so than the hydrobromic acid at a temperature of 125°–150°. While the presence of zinc chloride or zinc bromine as the second catalyzer increases the amount of ester formed, it yet remains true, as shown by the results given, that raising the temperature above the point where alcohol will just distil from the esterification flask will decrease the amount of benzoic ester produced in the case of either zinc chloride or zinc bromide, except where the zinc bromide is present in amount almost equal to the weight of benzoic acid taken. Zinc chloride in presence of hydrochloric acid is, however, a more efficient catalytic agent, both the hydrobromic acid and the zinc bromide being especially sensitive to any rise in temperature.

The amount of ethyl benzoate produced in experiments (1) and (3) of Table III is in the opposite ratio to the quantity of the ethyl chloride formed. Hence, the statement found in the literature that the efficiency of hydrochloric acid as a catalyzer is dependent upon the formation of nascent ethyl chloride would not seem to be borne out by these experiments.

It is to be noted, on the other hand, that zinc chloride, known to be one of the best catalyzers* in the formation of ethyl chloride from alcohol and hydrochloric acid, helps the esterification of benzoic acid. The extent to which hydrochloric acid has reacted to form ethyl chloride, either with or without zinc chloride, is seen on comparing (1) and (3) of Table III. The acid found in the esterification flasks in (1) and (2) of Table III shows a tendency to the accumulation of mineral acid in that flask. This accumulation is greater, naturally, at the lower temperatures. A similar tendency was observed at the temperature of 85°–90° in experiment (1) of Table I with hydrobromic acid. Since in (1) and (2) of Table III the same amount of alcoholic hydrochloric acid was employed, the temperature being the only marked difference, the results are directly comparable. It would seem possible that the accumulation of hydrochloric acid at the lower temperature might explain the greater yield of ester obtained. That is to say, the catalytic effect of hydrochloric acid to give ideal yields of ester depends upon a certain concentration of acid or of positive hydrogen ions, other conditions remaining the same. It would seem from these experiments that neither the concentration of the hydrochloric acid nor the concentration of the positive hydrogen ions can be the determining factor in esterification in the presence of zinc chloride, since it has been shown that alcoholic hydrochloric acid gives a much higher yield of ester in the presence of zinc chloride than when acting under precisely the same conditions without zinc chloride. The well known catalytic effect of zinc chloride on ethyl alcohol and hydrochloric acid to form ethyl chloride must have taken place and thus have diminished the concentration of the hydrochloric acid. Not only this, but in this action of alcohol and hydrochloric acid water has been produced, which would also be a hindrance to esterification. Yet the fact remains that in the presence of the lower concentration of hydrochloric acid, even with the water formed by alcohol and hydrochloric acid in the presence of zinc chloride, the zinc chloride is a most efficient catalytic agent in esterification.

Another proof that the amount of ester produced is not proportional to the concentration of the positive hydrogen ions present has been mentioned earlier in this paper, when it was noted that, under otherwise similar conditions, a small amount of sulphuric acid, which ionizes to a smaller extent than hydro-

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* Groves, Ann., clxxiv, 372.

chloric acid, which might be taken even in large amount, is a more efficient catalyzer in the production of ethyl benzoate.

It has been noted in previous papers on esterification and in this paper also, that an increase up to a certain limit in the amount of catalyzer present under given conditions has been helpful in every case studied. The increase in the amount of catalyzer beyond that limit is decidedly harmful, judging from the amount of ester formed. This would appear to be due to the fact that the catalyzers used, hydrochloric acid, zinc chloride, hydrobromic acid, zinc bromide, and sulphuric acid, have a strong affinity for water. It is also a fact, that each of the catalytic agents used reacts with alcohol of themselves to produce water, ethyl chloride being formed with hydrochloric acid, ethyl bromide with hydrobromic acid, and, ethyl ether with sulphuric acid. Consequently when they are present in large amounts together with a high-boiling point ester, absolute alcohol is not able to effect dehydration as completely as is necessary for complete esterification.

Hence it would seem that to esterify a given organic acid under most advantageous conditions for complete esterification it is necessary to determine experimentally the proper proportions of alcohol, the time of action, the most efficient catalyzers, and the most suitable temperature at which reagents and catalyzers interact. It has been shown that concentration of mineral acids as catalyzers does not control the esterification at the temperatures studied, and, further, that the best conditions of temperature for the formation either of ethyl chloride or of ethyl bromide are not ideal ones for esterification. When further experimental data upon this question are at hand it is hoped that the real function of catalyzers in esterification will be made known.

Art. XXXII.—*Researches on the Influence of Catalytic Agents in Ester Formation. The Effect of Certain Sulphates on Benzoic and Succinic Acids;* by I. K. Phelps, H. E. Palmer, and R. Smillie.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxxviii.]

In a former work* published in this Journal it has been shown that almost theoretical yields of succinic ethyl ester may be obtained by passing alcoholic vapor charged with dry hydrochloric acid into the flask containing the succinic acid. In a somewhat later paper† in this series of researches on esters, under the direction of one of us, it has been shown that theoretical yields of benzoic ethyl ester may be obtained from benzoic acid, using sulphuric acid as a catalyzer, while if no catalyzer be present, only a trace of the ester is produced under conditions otherwise precisely similar. Bogojawlensky‡ has studied the effect of various inorganic sulphates on the esterification of a number of organic acids, using as the indication of esterification the amount of ester produced by heating the mixture of acid, alcohol, and catalyzer on a return condenser. In the case of benzoic acid he obtained a yield of 92 per cent with a mixture of 30 grams of copper sulphate and 1 gram of sulphuric acid, while with sulphuric acid alone he obtained a yield of only 65 per cent, and with copper sulphate alone no ester whatever was formed.

In the work to be described the effect of various acid sulphates on the esterification of succinic and benzoic acids has been studied. Pure succinic acid was prepared by heating on a return condenser succinic ester, which boiled within 0·2°, with an equal volume of water and a few drops of nitric acid, and recrystallizing from water the pure succinic acid formed, as has been described in a previous paper§ in this Journal. In the case of the benzoic acid, the pure acid of commerce was used. The apparatus was the same as that illustrated and described in an earlier paper‖ in this Journal on the esterification of succinic acid. In all of the work absolute alcohol which had been made as free from water as possible by repeated distillations over lime was used. In all cases 40^{cm^3} of the absolute alcohol were put into the second flask together with the benzoic or succinic acid and catalyzer, and the remainder of the alcohol as vapor was run into the second flask from the first during the intervals of time indicated in the tables, the temperature of the mixture in the second flask being kept by means of an acid sulphate bath at 100°–110° during the action.

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* This Journal, xxiii, 368.

† This Journal, xxv, 39.

‡ Berichte, xxxviii, 3344.

§ This Journal, xxiii, 211.

‖ This Journal, xxiv, 194.

The catalyzers studied were the acid sulphates of potassium, ammonium, sodium, pyridine, and aniline. These were made, in the case of the inorganic salts, by heating the anhydrous neutral sulphates with the proper proportions of sulphuric acid in a porcelain crucible until the mass fused together, then grinding in an agate mortar. The organic sulphates were made by adding sulphuric acid in the proper proportions to the pyridine or aniline in the esterification flask in the case of the benzoic acid; in the case of the succinic acid, however, they were mixed before being put into the flask. The sodium sulphate, the potassium sulphate, the pyridine, and the aniline were the pure anhydrous material of commerce. Pure ammonium sulphate was prepared by treating in water solution with an excess of sodium hydroxide the ammonium salt precipitated by the action of hydrochloric acid on cyanacetic ester under the conditions shown in an earlier paper* in this Journal and catching the ammonia evolved on distillation in dilute sulphuric acid. The salt obtained by evaporating the solution, neutral to litmus, was recrystallized and dried.

The proportions of catalyzers used were chosen such that the amount of the sulphuric acid used to form the acid sulphates here was the same amount, or a multiple or submultiple of the amount, used as catalytic agent in the former paper† on the esterification of benzoic acid; that is to say, the concentrations of the hydrogen ions present during the esterification in the two researches were in molecular ratio.

Of the catalyzers studied, the acid pyridine sulphate was the only one which seemed to go entirely into solution during the esterification. Of the others, the acid ammonium sulphate was perhaps the most soluble, but it did not go entirely into solution, even in the case of the smallest amount which was used.

The succinic ester in experiments (1) to (7) inclusive of Table I was recovered, according to previous work,‡ by treating the crude ester in the esterification flask with an excess of solid potassium carbonate, and heating the flask fitted up for a vacuum distillation with a 100^{cm^3} Claisen flask as receiver, under a pressure of 15^{mm}, to 100°–110° on an acid potassium sulphate bath until no more carbon dioxide was evolved. The ester was then distilled under the same pressure—15^{mm}—, allowing a stream of cold water to strike the receiver continuously during the distillation. The distilled product was then redistilled, the lower boiling impurities being first removed by raising the temperature of the flask to 60° under a pressure of 15^{mm}, before the succinic ester was distilled and weighed. The succinic ester in the remaining experiments of Table I and the

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* This Journal, xxvi, 258.

† This Journal, xxv, 39.

‡ This Journal, xxvi, 253.

benzoic ester in all of the experiments of Table II, except where aniline acid sulphate was the catalyzer, were recovered by shaking out the ethereal solution of the impure ester from the esterification flask with a solution of sodium carbonate in a separating funnel containing a few pieces of ice and washing with a saturated solution of sodium chloride. The sodium carbonate and the sodium chloride wash waters were each extracted separately twice with fresh portions of ether to recover any portions of the ester that may have been carried along with them, and these ethereal solutions were added to the main mass of ester. The ether was distilled off on a water bath, after which the flask containing the ester was fitted for a vacuum distillation. The lower boiling impurities were removed by raising the temperature to 60° under a pressure of 15^{mm}; the ester was then distilled by heating to 140°–150° on an acid potassium sulphate bath under the same pressure—15^{mm}—, the receiver being cooled by allowing a stream of cold water to strike it continuously during the distillation. In the experiments where aniline acid sulphate was used, since the aniline formed on neutralization with sodium carbonate would distil over along with the benzoic ester, the aniline sulphate in experiments (27), (30), (31), and (32) of Table II was removed by first shaking up the ethereal solution of the crude ester with water in a separating funnel, and the recovery was then carried out in the usual manner. In experiments (28) and (29) of Table II all the material which would distil over below 150° under 15^{mm}

TABLE I.

No.	Succinic acid grm.	Catalyzer	grm.	Absolute alcohol cm³	Reaction time hr.	min.	Succinic ester Theory grm.	Found grm.	Per cent
1.	50	H_2SO_4	0·5	200	1	25	73·7	70·27	95·3
2.	50	"	0·5	200	1	30	73·7	70·00	95·0
3.	50	"	0·5	400	1	15	73·7	72·45	98·3
4.	50	"	0·5	400	2	0	73·7	72·70	98·6
5.	50	"	1·0	200	–	45	73·7	70·55	95·7
6.	50	"	1·0	200	1	0	73·7	70·72	96·0
7.	50	$KHSO_4$	0·694	200	1	10	73·7	33·40	45·3
8.	50	"	2·777	200	1	30	72·7	56·92	77·2
9.	50	"	5·554	200	–	55	73·7	36·74	49·9
10.	50	$(NH_4)HSO_4$	0·587	200	1	10	73·7	39·75	53·9
11.	50	"	2·348	200	1	15	73·7	59·85	81·2
12.	50	"	4·696	200	1	45	73·7	65·85	89·4
13.	50	$NaHSO_4$	4·899	200	1	15	73·7	69·25	94·0
14.	50	$C_5H_5N.H_2SO_4$	0·907	200	–	50	73·7	44·35	60·2
15.	50	"	0·907	200	1	0	73·7	42·85	58·1
16.	50	$C_6H_5NH_2.H_2SO_4$	0·975	200	1	0	73·7	1·50	2·0

pressure was collected first and afterward purified in the usual manner by treatment with ether.

From an inspection of the results of Table I it is evident that theoretical yields of succinic ester are obtained with sulphuric acid as a catalyzer, taking into consideration the loss of ester inherent in the process of recovery. In the case of acid potassium sulphate a greater yield is obtained by an increase, within limits, in the amount of catalyzer. This is shown by comparing (7) with (8). But if the catalyzer is present in larger amount, there tends to be a falling off in the yield, as is shown by comparing (8) with (9). Acid ammonium sulphate accelerates the esterification much more than acid potassium sulphate. An increase in the amount of acid ammonium sulphate increases the yield of ester. As is shown in experiment (13), acid sodium sulphate under the conditions of this experiment gives almost as good results as sulphuric acid alone.

In Table II are given the results with benzoic acid. It will be seen that acid potassium sulphate does not accelerate the esterification to any great extent, but that an increase in the quantity of the acid sulphate present up to a certain extent increases the yield, as appears in experiments (3) and (4); however, the presence of a still larger amount of the acid sulphate, as in experiments (5), (6), (7), and (8), seems to hinder the esterification; the esterification indeed seems to depend on conditions not yet completely understood. In the case of acid ammonium sulphate, it is evident that the yields increase both with the time of reaction and with the concentration of the catalyzer. From a comparison of (10), (11), and (14), in which the time of reaction was approximately the same, it is seen that the yields increase with the concentration of the catalyzer; and from a comparison of (9) with (10), (11) with (12), and (13) with (14), in each of which the amount of the catalyzer present was the same, it is evident that the yields of ester increase with the time of reaction. With acid sodium sulphate larger yields are obtained than with corresponding quantities of acid ammonium sulphate, but similarly the yields are increased as the reaction time is greater, as shown by comparing (15) with (16), (17) with (18), and (19) with (20), and also as the amount of catalyzer present is greater, as shown by comparing (15), (17) and (19), and further (16), (18) and (20) with each other. It is evident that neither the pyridine nor the aniline acid sulphates accelerate the esterification of benzoic acid to any great extent.

In comparing these results with the results which were obtained with sulphuric acid alone as a catalyzer in the former paper* in this Journal, it is evident that none of the acid sul-

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* This Journal, xxv, 39.

TABLE II.

No.	Benzoic acid grm.	Catalyzer	grm.	Absolute alcohol cm³	Reaction time hr.	Reaction time min.	Benzoic ester Theory grm.	Benzoic ester Found grm.	Benzoic ester Per cent
1.	50	$KHSO_4$	1·388	200	1	0	61·48	2·72	4·4
2.	50	"	1·388	200	2	45	61·48	9·64	15·7
3.	50	"	2·777	200	2	15	61·48	13·43	21·8
4.	50	"	2·777	200	3	15	61·48	19·21	31·3
5.	50	"	5·554	200	1	40	61·48	11·05	18·0
6.	50	"	5·554	200	1	45	61·48	5·75	9·4
7.	50	"	5·554	200	2	20	61·48	7·62	12·4
8.	50	"	5·554	200	2	30	61·48	10·02	16·3
9.	50	$(NH_4)HSO_4$	1·174	200	2	10	61·48	5·48	9·0
10.	50	"	1·174	200	3	15	61·48	8·69	14·1
11.	50	"	2·349	200	2	50	61·48	36·43	59·3
12.	50	"	2·349	200	3	50	61·48	41·30	67·2
13.	50	"	4·696	200	1	55	61·48	43·83	71·3
14.	50	"	4·696	200	3	0	61·48	48·56	79·0
15.	50	$NaHSO_4$	1·225	200	1	30	61·48	20·99	34·1
16.	50	"	1·225	200	3	0	61·48	40·43	65·8
17.	50	"	2·450	200	1	30	61·48	46·00	74·8
18.	50	"	2·450	200	3	0	61·48	58·69	95·5
19.	50	"	4·899	200	1	15	61·48	56·44	91·8
20.	50	"	4·899	200	3	0	61·48	60·58	98·5
21.	50	$C_5H_5N.H_2SO_4$	0·907	200	3	10	61·48	3·13	5·1
22.	50	"	0·907	200	4	0	61·48	5·00	8·1
23.	50	"	1·814	200	1	35	61·48	1·46	2·4
24.	50	"	1·814	200	2	0	61·48	2·77	4·5
25.	50	"	3·628	200	2	20	61·48	3·86	6·3
26.	50	"	3·628	200	3	10	61·48	3·63	5·9
27.	50	$C_6H_5NH_2.H_2SO_4$	0·975	200	1	50	61·48	1·39	2·3
28.	50	"	0·975	200	2	40	61·48	·56	0·9
29.	50	"	1·950	200	1	15	61·48	·37	0·6
30.	50	"	1·950	200	3	20	61·48	2·33	3·8
31.	50	"	3·900	200	1	15	61·48	2·60	4·2
32.	50	"	3·900	200	3	10	61·48	4 36	7·1

phates studied, when present in amounts of equal concentration of acid hydrogen, are as efficient in catalytic effect as sulphuric acid. Acid sodium sulphate is nearly catalytically equivalent; acid ammonium sulphate gives less effect; acid potassium sulphate considerably less; while acid pyridine and aniline sulphates are very poor catalyzers. The acid pyridine sulphate gives with succinic acid, which esterifies readily, distinctly more effect than acid aniline sulphate, but with benzoic acid, where esterification is more difficult, they give about the same effects.

Aside from the possibility of the acid sulphate in solution being the active catalytic agent, two explanations would seem obvious for the facts. First, that the catalytic effect is due in these experiments to a dissociation of the sodium and potassium acid sulphates into neutral sulphates and sulphuric acid, and of the nitrogen-containing sulphates into free base and sulphuric acid, this sulphuric acid so formed being the active catalytic agent. This explanation, however, fails in the case of the weakly basic aniline and pyridine salts. Second, since in most cases the salts used as catalyzers did not go into solution, and an increase in the amount of the salt used produced noticeable effects, it seems possible that the salts not in solution are active as contact agents. All that may be done, however, is to record our results until future experimentation, to be recorded in this series of papers on catalysis, will make clear the correct explanation of the facts under consideration.

ART. XXXIII.—*Researches on the Influence of Catalytic Agents in Ester Formation. The Esterification of Benzoic Acid with Certain Chlorides;* by I. K. and M. A. PHELPS and E. A. EDDY.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxxix.]

IN this Journal* in earlier work under the direction of one of us, the efficiency of zinc chloride with hydrochloric acid as a catalytic agent in the formation of the ethyl esters of benzoic, succinic, malonic, and cyanacetic acids has been shown. The esterification was carried on at a temperature of 100°–110° in an apparatus arranged for the purpose.

In the work given in this paper, in the specially arranged flasks illustrated in the work on succinic ester referred to, the catalytic action of certain chlorides in presence of hydrochloric acid in small amount in the esterification of benzoic acid with ethyl alcohol is brought into comparison with the similar action of zinc chloride with hydrochloric or of hydrochloric acid alone as catalytic agent. The esterification of this acid without a catalytic agent is shown to be almost none at all.

TABLE I.

No.	Benzoic acid grm.	Catalyzer	grm.	Abs. Alc. with HCl cm^3	per ct.	Time hr.	min.	Benzoic ester Theory grm.	Found grm.	per cent
(1)	50	----		300	---	3	--	61·48	trace	---
(2)	50	----		200	1·25	2	--	61·48	44·54	72·4
(3)	50	----		200	1·25	3	30	61·48	50·88	82·8
(4)	50	----		200	1·25	4	--	61·48	51·53	83·8
(5)	50	$ZnCl_2$	0·50	200	1·25	2	--	61·48	53·26	86·6
(6)	50	"	1·00	200	1·25	2	--	61·48	52·86	86·0
(7)	50	"	1·00	300	1·25	2	--	61·48	59·23	96·3
(8)	50	"	1·00	300	1·25	3	--	61·48	60·27	98·0
(9)	50	"	10·00	200	1·25	2	--	61·48	60·79	98·9
(10)	50	"	10·00	400	1·25	4	--	61·48	61·48	100·0
(11)	50	NaCl	0·86	200	1·25	2	--	61·48	38·14	62·0
(12)	50	"	8·60	200	1·25	2	--	61·48	42·00	68·3
(13)	50	KCl	1·09	200	1·25	2	--	61·48	43·94	71·5
(14)	50	"	10·90	200	1·25	2	--	61·48	37·23	60·6
(15)	50	LiCl	0·62	200	1·25	2	20	61·48	42·14	68·5
(16)	50	"	6·20	200	1·25	2	--	61·48	37·80	61·5
(17)	50	NH_4Cl	0·79	200	1·25	2	--	61·48	36·00	58·6
(18)	50	"	7·85	200	1·25	2	--	61·48	32·95	53·6
(19)	50	$CuCl_2$	1·00	200	1·25	2	20	61·48	53·91	87·7
(20)	50	"	9·87	200	1·25	3	20	61·48	59·62	97·0
(21)	50	$\left\{\begin{matrix} CuCl_2 \cdot \\ 2\,H_2O \end{matrix}\right\}$	12·58	200	1·25	2	--	61·48	59·05	96·1

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* This Journal, xxiv, 194; xxv, 39; xxvi, 143; xxvi, 264.

The pure benzoic acid of commerce was used in all the work recorded here. The alcohol was made as anhydrous as possible by repeated distillations over calcium oxide. A known amount of hydrochloric acid gas, dried by passing through concentrated sulphuric acid, was passed into a given weight of alcohol in the cold before diluting to definite concentration. The pure zinc chloride of commerce was made anhydrous by heating it to the melting point while a current of dry hydrochloric acid passed, then expelling the excess of hydrochloric acid by further heating before granulating. Potassium chloride was made pure by fusing potassium chlorate purified by recrystallization from hot water. Pure ammonium chloride was obtained by recrystallizing the product formed on treating with sodium hydroxide a water solution of ammonium salt precipitated in the conversion of cyanacetic ester to malonic ester in the procedure described in a former paper* in this Journal, and collecting in pure hydrochloric acid the ammonia gas

Table II.

No.	Benzoic acid	Catalyzer		Abs. Alc. with HCl		Time		Benzoic ester		
								Theory	Found	
	grm.		grm.	cm^3	per ct.	hr.	min.	grm.	grm.	per cent
(1)	50	$CaCl_2$	1·00	200	1.25	3	15	61·48	50·30	81·8
(2)	50	"	8·14	200	1·25	2	..	61·48	14·67	23·9
(3)	50	$SrCl_2$	1·16	200	1·25	2	10	61·48	32·63	53·1
(4)	50	"	11·60	200	1·25	2	5	61·48	32·34	52·6
(5)	50	$BaCl_2$	1·53	200	1·25	2	15	61·48	38·70	63·0
(6)	50	"	15·30	200	1·25	2	10	61·48	43·26	70·4
(7)	50	$HgCl_2$	1·00	200	1·25	3	15	61·48	41·11	67·9
(8)	50	"	1·98	200	1·25	2	..	61.48	51·70	84·1
(9)	50	"	19·80	200	1·25	2	..	61·48	60·65	98·7
(10)	50	Hg_2Cl_2	3·46	200	1·25	2	15	61·48	43·65	71·0
(11)	50	"	34·55	200	1·25	2	..	61·48	46·39	75·5
(12)	50	$\left\{\begin{matrix} AlCl_3. \\ 6\,H_2O \end{matrix}\right\}$	1·11	200	1·25	2	..	61.48	30·57	49·7
(13)	50	"	11·07	200	1·25	2	..	61·48	21·20	34·5
(14)	50	$\left\{\begin{matrix} MnCl_2. \\ 4\,H_2O \end{matrix}\right\}$	14·60	200	1·25	2	..	61·48	40·00	65·1
(15)	50	$SnCl_4$	0·96	200	1·25	3	20	61·48	54·91	89·3
(16)	50	"	9·60	200	1·25	2	..	61·48	58·86	95·7
(17)	50	"	9·60	200	1·25	3	..	61·48	60·00	97·8
(18)	50	$PbCl_2$	2·03	200	1·25	2	10	61·48	38·70	62·9
(19)	50	"	20·31	200	1·25	2	..	61·48	36·58	59·5
(20)	50	$SbCl_3$	1·10	200	1·25	3	15	61·48	51·98	84·6
(21)	50	"	11·00	200	1·25	2	20	61·48	58·80	95·6
(22)	50	$BiCl_3$	1·54	200	1·25	1	20	61·48	36·93	60·1
(23)	50	"	1·54	200	1·25	2	..	61·48	51·35	83·5
(24)	50	"	15·40	200	1·25	2	20	61·48	59·48	96·8

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* This Journal, xxvi, 143.

set free. The commercially pure chlorides of copper, barium, and strontium were made anhydrous by drying in an air-bath at 100°. Hydrous aluminium* chloride was prepared by precipitating the commercial salt in water solution with hydrochloric acid gas and drying the product in a desiccator. Lead chloride was made by recrystallizing and drying in a desiccator the product obtained by precipitating pure lead nitrate with hydrochloric acid. In case of all the other chlorides, the preparation of which is not given, the commercially pure material was used. The various chlorides were used in such molecular ratio that the chlorine should be present in the same amount as in the experiments with zinc chloride, which have been published previously.

The procedure is the same as has been given in the earlier work to which reference has been made. In the experiments alcohol, with hydrochloric acid in the concentrations indicated in the tables, was driven over as vapor from a 500^{cm^3} round-bottomed flask into the mixture of benzoic acid and alcoholic hydrochloric acid containing the additional catalyzer in a second 500^{cm^3} round-bottomed flask carrying a modified Hempel column through which vapors passed to a condenser. The temperature of the second flask was kept between 100° and 110°.

In most cases the crude ester from the esterification was recovered by extraction with ether in the manner outlined in earlier work on catalysis in ester formation. Where on account of a large amount of such catalyzers as bismuth, antimony, or tin chloride, an ether extraction would be impracticable, the mass of ester with the low-boiling products was distilled from the esterification flask to a 100^{cm^3} Claisen flask before neutralizing with potassium carbonate and recovering by the procedure† published by us earlier in this Journal.

It is evident from an inspection of the results given in the tables that, as has been seen in all the previous work on esterification, the amount of ester formed, other conditions remaining the same, varies with the kind and amount of the catalyzers present, with the time of action, and with the quantity of alcohol. Certain of the catalyzers appeared under the conditions of experimentation to dissolve completely in the alcoholic mixture. This was observed in the use of the chlorides of zinc, lithium and tin. In the cases of the chorides of copper, calcium and mercury in the higher condition the smaller amounts only seemed to go into solution completely. Aluminium chloride in the smaller amount used went into solution at first but later in the experiment was precipitated out. The

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* Gooch and Havens, this Journal, ii, 416.

† This Journal, xxvi, 253.

bismuth and antimony chlorides with the hydrochloric acid in the concentration taken did not give a clear solution in any case, as is also true of all the other chlorides employed as catalyzers. In interpreting the results given in the tables some slight account should be taken of the fact of the insolubility of the salts used, especially where the amount is large. This is obvious when it is considered that a homogenous mixture could not be maintained by the agitation of the liquid as caused by the bubbling of the alcoholic mixture through the mass in the esterification flask.

The action of the catalyzers can be seen by comparing with each other the experiments given in Tables I and II. Evidently zinc chloride present in the larger amount as a second catalyzer with the small per cent of hydrochloric acid causes the esterification of benzoic acid with ethyl alcohol in largest amounts although copper or tin chloride present in molecular ratio for chlorine content are almost equally good. The presence of more than two grams of water of crystallization with the copper chloride in experiments (21) of Table I would appear to have produced no noticeable reduction in the amount of ester produced by the anhydrous salt taken in experiment (20) of Table I, where the yield is only 0·9 per cent better, although the time of action is decidedly longer. The chlorides of bismuth, antimony, and mercury in the higher condition of oxidation seem to be about equally efficient as catalytic agents. They are nearly as effective in their action as either zinc, copper, or tin chloride. Calcium chloride present in the smaller amount seems to be without effect, as is seen when experiment (3) of Table I is compared with experiment (3) of Table II. In larger amount it hinders esterification to a marked degree. Strontium chloride in the amounts taken seems to hinder esterification but not to such an extent as did the larger amount of calcium chloride. Barium chloride seems to hinder esterification slightly. The chlorides of lead, mercury in the lower condition of oxidation, manganese, and potassium at least do not assist esterification if their action is not entirely without effect. It was noticed that from the mercurous chloride small amounts of mercury distilled into the condenser, indicating decomposition of the mercurous chloride under the conditions of esterification. Sodium chloride appears to hinder esterification slightly, lithium chloride hinders more, ammonium chloride still more, and aluminium chloride more than any of the chlorides studied here except calcium when present in the larger amount.

It is worthy of note that each chloride, and, moreover, different amounts of the same chloride, tend to show an individual and characteristic effect as a catalytic agent with a small amount of hydrochloric acid in the formation of ethyl benzoic ester from benzoic acid and ethyl alcohol. However, it seems to be true that certain of the chlorides may be grouped according to their behavior as catalytic agents here. Although from the theoretical considerations some of the catalytic effects shown in this paper might have been predicted, such as the accelerating action of antimony and bismuth chlorides and the lack of action of potassium chloride, certain of the other effects could not, so far as we are aware, have been predicted. The action of cupric and mercuric chlorides in producing large amounts of ester or of lithium chloride in hindering esterification could not have been predicted. Further, Claisen* in the study of catalytic effects in the formation of acetals from aldehydes and ketones, found that ammonium chloride was an efficient catalytic agent and that the alkali chlorides were without action. It becomes evident then that catalytic effects are not only specific and individual for different chlorides and for different amounts of this same chloride, but, also, each catalytic agent gives a characteristic effect, either positive, negative, or neutral, in each specific kind of chemical change.

All of the results given here were obtained under conditions of temperature ranging from 100 to 110°. What differences may be found at other temperatures will be determined and given later. It is obviously too early in the study of catalysis to complete our imperfect theory for such effects as are shown in the contribution to the study of catalysis given in this paper.

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* Berichte, xl, 3903.

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Art. XXXIV.—*Buried Channels Beneath the Hudson and its Tributaries;* by J. F. Kemp.

The Hudson river has afforded to previous observers problems of more than ordinary physiographic interest. The dissected peneplain, which the Highlands about West Point present to those who look abroad from any of the neighboring summits, is one of the best exhibitions of this land-form, easily accessible to routes of travel. Although the Highlands appear from the surface of the river to be a range of mountains, from the summits themselves the group becomes an incised plateau forming part of the Schooley peneplain, first identified in New Jersey to the southwest by W. M. Davis and J. W. Wood, Jr.* This peneplain probably marked the closing of a cycle of drainage fairly coincident with the Cretaceous period. An uplift subsequently revived the streams and the Tertiary cycle began. The traces of the latter are still visible along the Hudson in rocky terraces, which stand out with marked conformity as a series of shelves, best shown in the western bank and especially prominent in the cold season. A walk from Fishkill to Peekskill on a crisp winter's day, when the foliage no longer masks the relief, will serve to bring out many points not visible in the months of leaves.

Having excavated the broader valley outlined by these shelves, the river was obviously again revived and eroded, within the older limits, the narrower channel of whose details we are just now gaining possession. They piece out in part a missing or fragmentary chapter in its history, the one which relates to the time antedating the invasion of the continental glacier. As will be shown, they corroborate the previously

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* The Geographic Development of Northern New Jersey, Proc. Boston Soc. Nat. Hist., xxiv, 365, 1890. Also W. M. Davis, The Catskill Delta in the post-Glacial Hudson Estuary, idem., xxv, 318, 1892.

inferred elevation of the land which we had been led to assume from the general phenomena of ice accumulation and from the specific characters of the submarine valley of the Hudson, whose recognition even before 1863 by the late Professor J. D. Dana marks one of the many acute observations and inferences regarding the local geology which we owe to his tireless activity. Professor Dana, however, had but imperfect data and consequently an inadequate idea of the depths involved.* Mr. A. Lindenkohl of the U. S. Coast and Geodetic Survey, and with more extended soundings, took up the question anew in 1885 and 1891.† A canyon was demonstrated in the continental shelf which about 50 miles off Sandy Hook was 2400 ft. below the neighboring sea-bottom, there found at a depth of 420 ft. Beyond this point and along the course of the submerged channel, soundings of much less depth were met, and for some years the inference was drawn that a bar, of inexplicable character and apparently too far out to be a terminal moraine, crossed the mouth of the canyon and filled it up. Subsequently more numerous soundings proved this apparent bar to be due to a sharp southerly bend in the canyon, whose course had hitherto been southeast to east by south, and that it extended with increasing depth to the edge of the continental shelf. These latter features have been especially brought out and emphasized by J. W. Spencer in a valuable series of papers discussing off-shore phenomena in the sea-bottom, and best summarized in this connection in the reference given below,‡ in which will also be found a review of earlier work. Dr. Spencer demonstrates the existence of the canyon down to 9000 ft. below the surface. This aspect of the subject will not be pursued further in this paper, the object being merely to remind a reader that these conditions exist off the mouth of the Hudson and that they have an interesting connection with the phenomena of its land-channel. The most obvious suggestion in explanation is the elevation of the land, yet the amount of elevation required is a bit staggering. We are reminded of the alternative view, not without its advocates, that the land may have remained stable while the ocean drew off to the southern hemisphere and by lowering the sea-level established equivalent drainage relations.§

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* See the Manual of Geology, 1st ed., 1863, p. 441, where the depth at about 80 miles from Sandy Hook is given as only 720 ft.

† Geology of the Sea-Bottom in the approaches to New York Bay, this Journal, xxix, 475, 1885. Notes on the Submarine Channel of the Hudson River, and other evidences of Post-Glacial Subsidence of the Middle Atlantic Coast Region, this Journal, xli, 489, 1891.

‡ The Submarine Great Canyon of the Hudson River, this Journal, January, 1905, 1–15.

§ H. W. Pearson contributed a series of papers upon this point to the supplement of the Scientific American, early in 1908.

Others have been impressed with the possibilities of submarine erosion by a current along the sea-bottom, and have sought in this way to avoid the necessity of assuming an improbable elevation.*

The submarine channel is first and somewhat faintly discernible about 5 miles off Sandy Hook. From this point north it is submerged in later sediments and is unrecognizable. From Princes Bay on the Staten Island shore outward the strata are the soft and incoherent beds of the Mesozoic and Tertiary, but from Princes Bay northward to Cornwall-on-Hudson the hard metamorphic and plutonic rocks form the bottom; still farther north are the scarcely less resistant slates, sandstones, and limestones of the Ordovician and Cambrian. In these two portions erosion must have proceeded more slowly.

Turning from the pre-Glacial Hudson for the moment, the post-Glacial work may be briefly reviewed in order to make clear the state of our knowledge from this point of view. Upon the later deposits much the most detailed work has been done. It was early recognized that a period of subsidence had followed the retreat of the ice sheet, making of the valley a quiet estuary in which the fine Champlain clays were laid down. Upon these and after an uplift the very prominent gravel and sand deltas were built up. Subsequent elevation brought about their bisection and the exposure of the clays well above tide-level. F. J. H. Merrill has traced these and their relations from New York to Albany.†

The local details of terraces, deltas, moraines, etc. have been elaborated in still greater detail by C. E. Peet‡ of the Department of Geology at the University of Chicago, and by J. B. Woodworth§ under the auspices of the N. Y. State Geological Survey. Both these writers treat the interesting question of the old relations of Lake Champlain and the Hudson, but these later problems do not bear very closely on the points here to be elaborated. These concern the drainage relations in that critical stage when the Glacial epoch was approaching, and they give us some insight into the attitude of land and sea during this and later time.

The data utilized in this paper were gathered by the Board of Water Supply of the City of New York and in connection

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* This alternative is briefly discussed with citations in J. B. Woodworth's Ancient Water Levels of the Champlain and Hudson Valleys, Bull. 84, N. Y. State Museum, 71–72, 1905.

† Post-Glacial History of the Hudson River Valley, this Journal, xli, 460, 1891. Origin of the Gorge of the Hudson River, Bull. Geol. Soc. Amer., x, 498, 1899.

‡ Glacial and Post-Glacial History of the Hudson and Champlain Valleys, Jour. Geol., xii, 415-469, 617-660, 1904.

§ Ancient Water Levels of the Champlain and Hudson Valleys, Bull. 84, N. Y. State Museum, 1905.

with the new sources of water which are to be tapped from Esopus Creek in the Catskills for the rapidly growing population of the metropolis. The writer would express his acknowledgments to J. Waldo Smith, C.E., Chief Engineer, for permission to use the data in this way, and to Robert Ridgway, C.E., Department Engineer of the Northern Department, within whose territory nearly all the ground here covered is embraced. From the Division Engineers, A. A. Sproul, W. E. Swift, L. E. Brink, L. White and C. E. Davis, and from J. F. Sanborn in charge of the geological features and records, every facility has been received. Alfred D. Flinn, C.E., Department Engineer of Headquarters, has written of the Storm King crossing.* The writer has constantly worked with his colleague, Dr. C. P. Berkey,† in the field and has discussed results in the laboratory. The interpretations here given and the details of local geology are based upon the observations and inferences of both.

The General Line of the Aqueduct.—The main reservoir for the new supply will be developed by a huge masonry dam which will cross and impound Esopus Creek at the Olive Bridge site, a few miles below Shokan in Ulster County. The dam is to be in the more open country southeast of the Catskills, which are in full view a few miles away. At this point the Esopus is in a deep post-glacial gorge in the Hamilton‡ flagstones, which dip at a flat angle to the northwest and are cut into extremely regular blocks by a most remarkable series of joints. The master joints average N. 21 E.; the next in prominence, N. 71 W., while rarely there are others at N. 9 W. and N. 8 E.

The spillway of the dam will be at 580 ft., so that wherever in its course to the city the aqueduct crosses a valley, the water must be conducted in a pressure tunnel. Since bedrock tunnels for a clear cross-section of fifteen feet or more are far cheaper than steel pipes, it has been of prime importance to keep the aqueduct in solid rock, with sufficient cover wherever it dipped below grade; at the same time a tunnel whose bursting pressure is from within, rather than from

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* Explorations for Hudson River Crossing of the Catskill Aqueduct, New York City, Engineering News, April 2, p. 358, 1908.

† Early in the development of the explorations the writer was appointed consulting geologist to the Board. About the same time Prof. W. O. Crosby received a similar commission and a year later Dr. C. P. Berkey. While the writer has often worked in association with Dr. Berkey, our reports have been made in entire independence of those of Prof. Crosby, with whose results the writer is not familiar.

‡ The name Hamilton is here used in a general sense to include the Hamilton, Sherburne and Ithaca. The section embraces practically uniform sandstones and shales, almost if not quite devoid of index fossils, and with no sharp demarcation. It is quite certain, however, that the higher members are included.

without, presents certain novel and interesting problems and makes solid rock a fundamental necessity. In the locations the geologist is of well-nigh indispensable service to the engineer.

In the course of its line from the reservoir to New York, the aqueduct has to cross the following principal depressions: Rondout Cr. 160′ A.T.; Wallkill River 150′ A.T.; Moodna Cr. 90′ A.T.; Hudson River 0 A.T., which it reaches at El. 400+; Sprout Br. 145′ A.T. and Peekskill Cr. 60′ A.T. Before the final line was selected several tentative ones were explored, giving us the records of depressed channels not on the final line. At the outset wash-borings alone were used, but when later tested by the diamond and calyx drills they were found to be entirely unreliable. On the basis of their records a bowlder might be taken for the bed-rock as easily as not. The sections subsequently plotted on wash-borings, therefore, show merely that the bed rock is presumably deeper yet. To this extent they are, however, of value.

The geological section inevitably crossed is complex both in number of formations and in their structural relations. Beginning on the north in the flat Hamilton beds of the Devonian, the tunnel in passing beneath Rondout Creek penetrates the full section of the Helderberg series as shown in fig. 4 together with the Shawangunk grit, in and west of the mountains of the same name. It passes beneath Bonticou Crag, three or four miles north of Lake Mohonk, and thence through or over Hudson River slates until it reaches the Archean granite of Storm King mountain, here thrust up on the slates by a reversed fault. The tunnel dips under the Hudson in the granite entirely, and rises on the east bank in the same rock. Thence it continues over or through the sedimentary gneisses, marbles, etc., of the Grenville,* but at Peekskill Creek also cuts the Poughquag quartzite and Wappinger limestone of the Cambro-Ordovician. These formations have all dips from flat to vertical; are folded often in a violent way; and are faulted in a very complicated manner. Several of the tentative lines had more to do with the Wappinger limestone than the one finally selected and therefore this formation appears along the more northerly routes.

The General Drainage Relations.—The relations of the tributary streams to the Hudson north of the Highlands are in some respects peculiar. Those on the west bank present

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*After consultation with Dr. C. P. Berkey, who has done much detailed mapping in the Highlands, and after going over together the exposures both in this locality and in the eastern Adirondacks, this name, hitherto current in the more northerly region, is employed, in the belief that the formations are essentially equivalent.

FIG. 1.

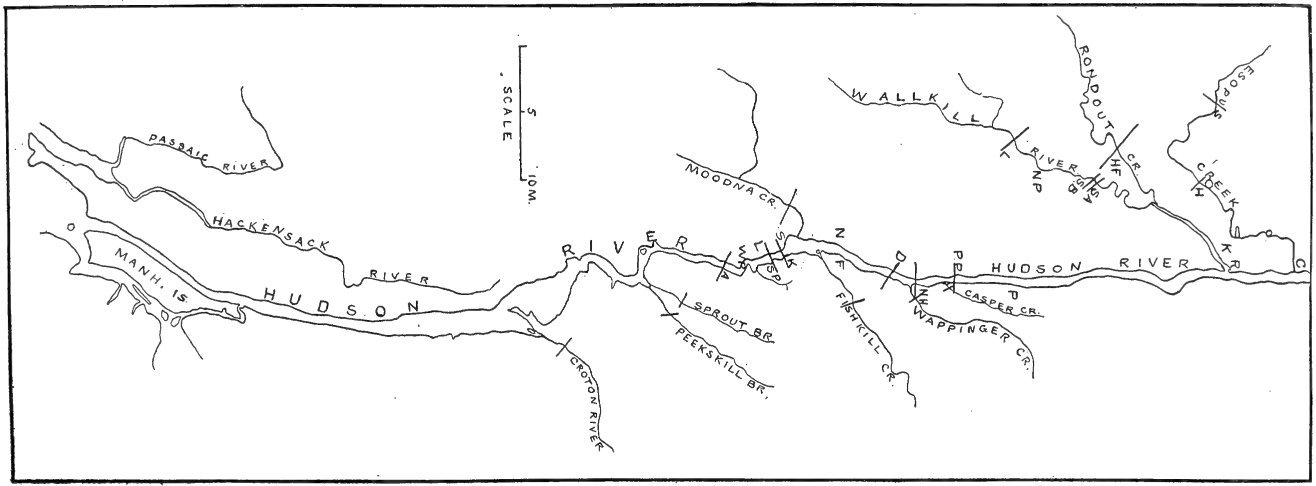

FIG. 1. General map to show the locations of the crossings tested. A. Arden Point; C. Catskill Village; D. Danskammer; F. Fishkill Landing; H. Hurley; H.F. High Falls; K. Kingston; L. Libertyville; L.S.P. Little Stony Point; N. Newburg; N.H. New Hamburg; N.P. New Paltz; P. Poughkeepsie; P.P. Peggs Point; R. Rondout; S.A. Springtown A; S.B. Springtown B; S.K. Storm King; W.P. West Point.

an apparent reversal of drainage—that is they come in from the southwest and turn a sharp corner so as to flow to the sea in a southerly direction. The lower Esopus, the Rondout, the Wallkill and the Moodna all conform to this rule, as will be seen from fig. 1, while on the east bank the streams enter from the northeast. The relations are due to the geological structure. The strike of the rocks and the trend of the ridges are northeast and southwest. The Shawangunk ridge, the wonderfully folded and faulted Helderberg strata and the Archean Highlands are particularly influential. The upper waters of Esopus Creek come across the flat opposing dip of the Hamilton until they strike the folded lower strata and then make the turn. In the upper waters the joints are the chief structural influences, the stream on the whole adopting a resultant between the N. 21 E. and the N. 71 W., although sometimes on one set, sometimes on the other.

Tributaries on the West Bank.

The Tongore Crossing of the Esopus.—This is shown in fig. 2, which is drawn looking down stream or southeast. The stream at this point flows nearly east, along the minor series of joints N. 71 W. It has cut a steep gorge in the flagstones and shales to the 320 ft. contour. On the south bank the bed-rock rises above the 550 ft. contour and is often exposed, but on the north bank drift conceals all the rock. A series of borings has shown the cover to vary from 60 to 250 ft., and that a buried channel exists at 240 ft. A.T., or about 70 ft. below the present river. Its sides have gentle slopes and its profile is that of a much more mature stream than the present Esopus, from which it is distant about 2,000 ft. to the northeast. Several other crossings have also been explored, but this one will serve to illustrate the relations in altitude.

Fig. 2.

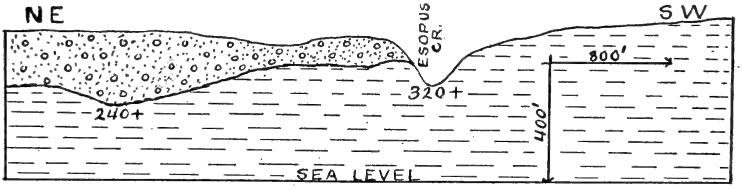

Fig. 2. The Esopus channel. The bed-rock is the Hamilton flagstones and shales.

The Hurley Crossing of the Esopus.—In its southeasterly course the Esopus breaks through the Hamilton escarpment and strikes a broad open valley, with all the characteristics of an old lake bottom, located upon some well-developed valley

Fig. 3.

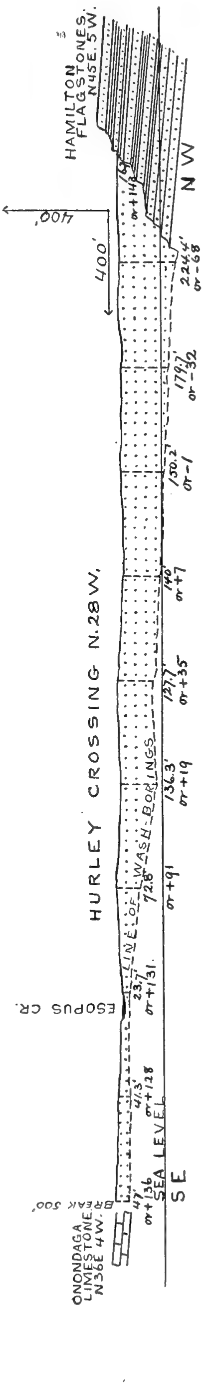

Fig. 3. The Hurley Crossing of the present Esopus and of the Pliocene Kripplebush.

of pre-glacial drainage to which fuller reference is subsequently made. It turns a right angle in this and passes northeasterly. Near Hurley station on the New York, Ontario and Western Railway, a series of borings was made across the valley with the results shown in fig. 3. On the northwest side is the abrupt escarpment of the Hamilton with characteristic shelf and talus outline. For nearly a mile to the southeast the sandy level extends and the first outcrops encountered are those of the Onondaga (old name Corniferous) limestone with a very flat northwesterly dip. The wash-borings, which are probably a fair indication of the bed-rock, reveal a surface which corresponds very closely to the dip of the strata. Apparently the pre-glacial stream followed down the dip of the limestone against the basset edges of the shales and sandstones, sapping them until it had attained a depth of 68 ft. below the present sea-level, and showing that there must have been a correspondingly greater elevation of the land. In the closing stages of the ice epoch some barrier must have impounded the water in this valley and have caused the accumulation of the sands.

There are some very interesting questions raised by the relations of the pre-glacial Esopus and pre-glacial Rondout. The former after its northeasterly bend proceeds to the Hudson along the general prolongation of the latter, which turns at Rosendale through a high and abrupt ridge of the Helderberg strata, with quite precipitous sides, and joins the Wallkill. The combined streams then reach the Hudson through an estuary with steep rocky sides and apparently much freshened up by the ice-sheet, if, as seems unavoidable, it is of greater geological age.

The High Falls Crossing of the Rondout Valley.—As shown in fig. 4, the aqueduct reaches the Rondout valley on the northwest side at 500 ft. grade. Beyond this point for over four miles it must utilize a pressure tunnel known as the Rondout Siphon. The borings reveal a buried channel on the northwestern part of the valley sunk in the bed-rock to 80+, or 270 ft. below the present surface. As this is near the hamlet of Kripplebush we have called it the Kripplebush channel. The cores prove that we have a fault, probably a normal one, upon which the stream was located at the time it was overwhelmed. It had worked down the Onondaga limestone against the basset edges of the Hamilton just as had the old-time stream at the Hurley crossing, and then it had been arrested and obliterated by the drift. We have no further records of this stream, but along the line of the siphon and after leaving the valley of the Kripplebush there is only a thin cover of drift, with frequent outcrops before the next depression is reached. Then about two miles farther east-

Fig. 4.

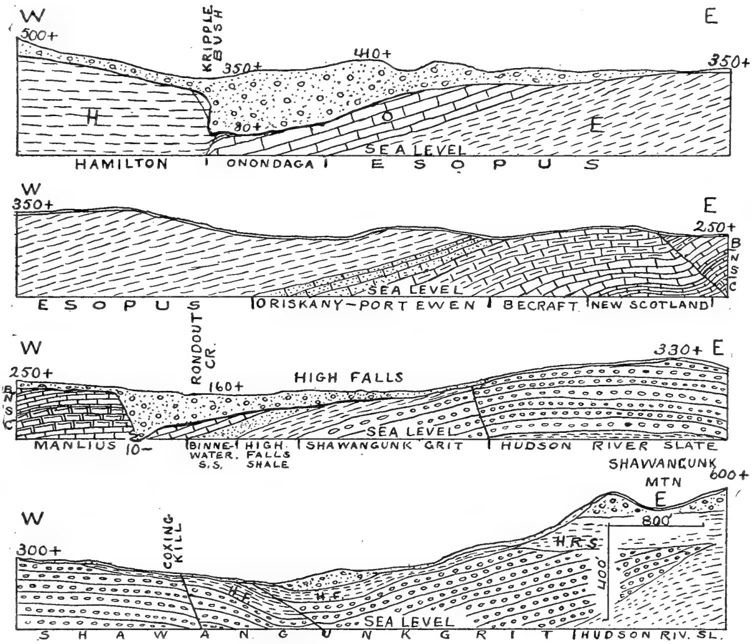

Fig. 4. The Rondout Crossing near High Falls. B. Becraft limestone; N.S. New Scotland limestone; C. Coeymans limestone; H.F. High Falls shale; H.R.S. Hudson River slate. The sections are continuous.

ward is the present Rondout Creek, now flowing on drift at the line of the section. A little to the north, however, it swerves eastward and cascades over a ledge of Manlius limestone. About 400 ft. west of the point where the siphon passes below the present stream, the drill revealed an old, buried channel with a bottom at minus 10, or beneath somewhat over 200 ft. of drift. The pre-Glacial stream had evidently followed down a dip slope of Manlius, sapping the edges of the Coeymans (labeled C in the figure) and New Scotland limestones until it also was obliterated by the drift. We think it had left a projecting ledge of Manlius as shown in the figure, because the drill passed from drift into limestone and then into drift again before it caught the bed-rock. The Manlius is the formation containing the waterlime beds, and its subdivision into the Rondout, Cobleskill, Rosendale and Manlius proper has not been attempted here. Somewhat contrary to one's natural expectations, it (an argillaceous variety) is the formation containing the fissures and caves of the region, whereas one would be inclined to look for these rather in the Becraft, which is a very pure limestone. The ancient Rondout Creek moreover, somewhat strangely, seems to have followed the Manlius rather than the hard Shawangunk grit with its soft overlying High Falls shales, which were cut farther east.

Of the further relations of this buried channel we have no records. The Hurley crossing showed a depth of minus 68, so that so far as gradient is concerned it might have gone out this way.

A mile and a quarter eastward there is a patch of drift in a little synclinal valley of High Falls shale, whose bottom stands at 160 plus, but the depression is of no great consequence.

The Wallkill Crossings.—After passing through the Shawangunk ridge by a tunnel at grade, the aqueduct turns southwest along the surface and crosses the Wallkill valley near the little hamlet of Libertyville, three miles southwest of New Paltz. The entire tunnel will be in Hudson River slates. Before this line was selected, however, two lines of borings were made near Springtown about three miles north of New Paltz and several additional ones in or near the town, which are not here used, as they introduce no essential change in the conclusions. The two Springtown lines are rather less than a mile apart and are called, on fig. 5, Springtown A and Springtown B. In the former a buried channel was found at minus 79 almost beneath the present river, which stands at plus 150 or about 229 feet above. The old channel is filled with drift. About a half mile westward a small depression was detected at plus 50, evidently marking a tributary and smaller stream, separated by a divide of less than 40 ft.

The Springtown B profile found the old channel of the Wallkill about a thousand feet east of the present one and just at sea-level. The old valley is broad and open with a fairly mature aspect. The western channel is also shown but at 4000 ft. distance and at plus 65, or 15 ft. above the more northerly section. A divide of 150 ft. separated it from the Wallkill, and we cannot but infer that it was coming down to the larger stream from a source to the southwest.

It is a striking fact that the Pliocene Wallkill dropped 79 ft. in the mile or less from Line A to Line B and that its valley narrowed appreciably. It may have been on softer slates in the southern section and, encountering the reefs of sandstone characteristic of the Hudson River series, cascaded over them to lower reaches on the north. Springtown A is the last record which we have of it. The present Wallkill after combining with Rondout creek forms the Rondout river and enters the Hudson in the deep estuarine gorge at the city of Rondout, which has been previously mentioned. The rock bottom of this estuary must lie at a goodly depth below minus 79.

FIG. 5.

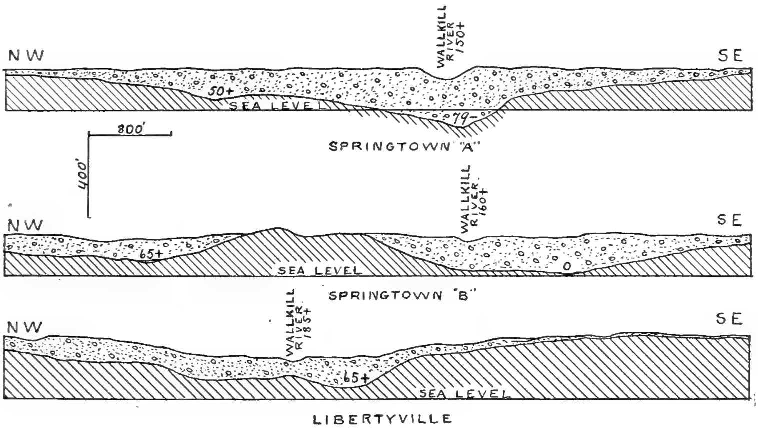

FIG. 5. Crossings of the Wallkill river near Springtown and Libertyville.

The Libertyville section is six or eight miles southwest of the Springtown crossings. It found the Pliocene channel some 600 ft. east of the present Wallkill and 120 ft. below it, or at plus 65. Therefore in the intervening stretch, while the modern Wallkill in its meandering course over the drift-filled valley drops 25 ft. the ancient river descended 65 ft. and thus had a fairly steep gradient. It must have been feeling the effects of uplift, although the profiles do not indicate any notable incision. In this section the westerly tributary is not pronounced. Its

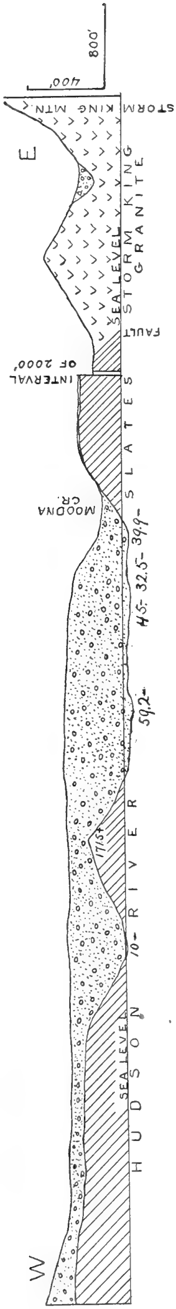

Fig. 6.

Fig. 6. The Moodna Crossing.

source must either have been passed or else it still lies beneath the drift farther west than it was necessary to bore.

The Moodna Crossing.—Having passed the Wallkill valley by a siphon, the aqueduct reaches sufficiently elevated ground to make a long course to the south at grade. Its first depression is at Moodna creek, which enters the Hudson just north of Cornwall. The Moodna proper comes in from the west, but it receives an important tributary, Woodbury creek, which drains the valley between Schunemunk mountain and the Highlands. In the three miles before it discharges into the Hudson the Moodna has cut a deep gorge in exceedingly heavy drift, with huge bowlders of very impressive size and extremely troublesome to penetrate with either the calyx or the diamond drills.

The details of the Moodna crossing are shown in fig. 6. The present creek is in the drift but very near the southern emergence of slates, and at about the 100 ft. contour. For a half mile to the west the drills have shown a very even floor with a maximum depression at minus 59·2 beneath 360 ft. of drift. A divide then rises of sharp outline, beyond which is another old channel reaching minus 10. The surprising thing about this section lies in the fact that two or three miles away is the gorge of the Hudson with a depth below of minus 600 ft. We have therefore been slow to admit that there is not somewhere in this section an incised notch through which the ancient drainage of the country to the southwest must have been poured without leaving a hanging valley 550 ft. above its master depression. Still, careful search and fairly close-set holes have failed to locate it. Somewhat the same relationships with the Hudson gorge are shown by other tributaries, such as the Wappinger, and Fishkill and the Croton, as will be later brought out.

Rather more than half a mile southeast of the present Moodna, the siphon will cross the impressive reversed fault which has brought the Archean granite to rest upon the Hudson slate, as is clearly exposed at one significant locality. A small drift-filled channel has been met in the granite, but it is only worthy of passing remark. Thence to the Storm King crossing the aqueduct is located at grade.

FIG. 7.

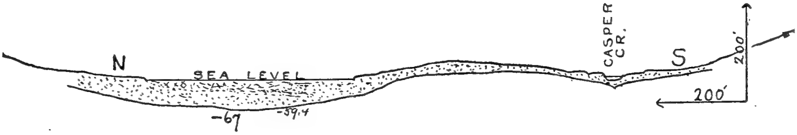

FIG. 7. The Casper Creek Crossing.

Tributaries on the East Bank.

Casper Creek.—The most northerly of the eastern tributaries is Casper Creek, which enters the Hudson six miles below Poughkeepsie. It was encountered by the proposed Peggs Point route and tested with wash-borings, but as only peat, sand, and at the bottom some gravel, were encountered the results are fairly reliable. They are plotted in fig. 7. The lowest point was minus 67. The section passed from Wappinger limestone on the north to Hudson River slate on the south. The section is perhaps half a mile from the Hudson.

FIG. 8.

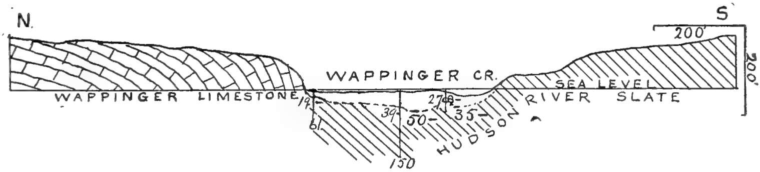

FIG. 8. The Wappinger Creek Crossing.

Wappinger Creek.—This good-sized stream enters the Hudson just south of New Hamburg. Two miles back it yields a fine water power by a series of cascades over Hudson River slates, with a fall of 60 or 70 ft. The water power supports the village of Wappinger Falls. Thence to the river it forms an estuary at tide level. At New Hamburg it lies along the contact of the slates and limestone, but while the limestone appears with steep dips in the north bank, the drill has shown slate beneath the water. There may be a faulted contact; the relations are obscure. As shown in fig. 8, one wash-boring reached 50 feet below tide, and of the three core borings, the deepest was minus 39. These comparatively shallow depths, taken very near the Hudson itself, are interesting parallels with the Moodna and Casper crossings, and are indicative of hanging valleys of somewhat striking altitude, and with apparently abrupt drops to the gorge of the Hudson.

Fishkill Creek.—Fishkill Creek enters the Hudson just south of Fishkill Landing, an important town on the river immediately opposite Newburg. Within two miles of its mouth it cascades over the Hudson River slates and is obviously off the line of its Pliocene channel. A proposed line for the aqueduct, but one which was afterwards abandoned, crossed it just east of Fishkill village, a small settlement five miles back from the river and not to be confounded with Fishkill Landing. The line crossed the creek in a direction a little east of south and at a flat area of meadow land where the stream was split into three parts. The profile is given in fig. 9. The entire section is drift-covered, but the two coreholes revealed the Wappinger limestone, as had been anticipated. The deepest channel was found at −40, but strangely enough the drill after penetrating about 8 ft. of limestone met fine yellow sand, in which it continued for over 60 ft. until the hole was abandoned. This was interpreted as a crevice in the limestone filled with decomposition products. The conventional signs in fig. 9 are not intended to indicate the dip of the limestone, but merely its presence. The dip is unknown to the writer. A short distance to the southeast the limestone gives place to the Archean, but directly south it extends as a faulted block much farther into the Highlands.

FIG. 9.

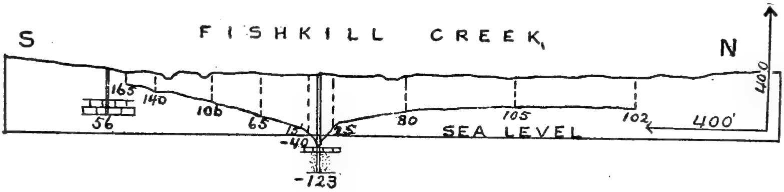

FIG. 9. The Fishkill Brook Crossing.

The Fishkill crossing is much farther back from the Hudson than the Wappinger, but its depth is only 10 ft. less.

Sprout Brook.—In its passage of the Highlands the aqueduct does not encounter any badly depressed area. Foundry brook, east of Cold Spring, has occasioned some drilling but has revealed no important physiographic data. Spring Brook is on the southern side and, with Peekskill brook, flows into

Annsville cove just north of Peekskill. Along this line is the crucial area in the interpretation of the geology of the Highlands, as has already been discussed by C. P. Berkey.*

The crossing is about three miles from the Hudson, in a narrow and rather steep-sided valley. Archean gneiss forms the hills, but after a concealed strip on each side the drill revealed white marble in the bottom, beneath 125 ft. and less of drift. The bottom of the buried channel was caught at −8, as shown in fig. 10. This is less than the last two, but the stream is hardly as large. The stream evidently selected the easily eroded limestone in preference to the harder gneisses.

Fig. 10.

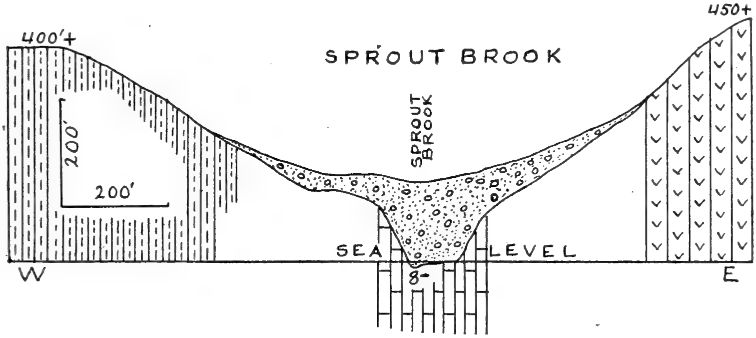

Fig. 10. The Sprout Brook Crossing. Sedimentary gneiss on the west; marble in the valley; granite gneiss on the east.

Fig. 11.

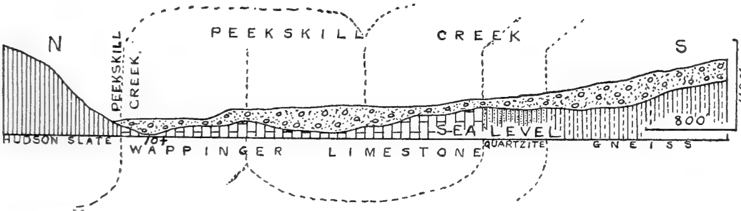

Fig. 11. The Peekskill Brook Crossing.

Peekskill Creek.—East of a steep divide from Sprout Brook lies the valley of Peekskill Creek, a somewhat larger stream and one in a broader valley. On the north side is the Hudson River slate at a steep angle and in an abrupt hillside. The present creek flows upon drift at its foot. Thence to the south for over a mile there are no exposures and the geology must

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* Structural and Stratigraphic Features of the Basal Gneisses of the Highlands, Bulletin 107, N. Y. State Museum, 361, 1907.

be interpreted by the drill-records, of which there are a satisfactory number. Figure 11 illustrates the section interpreted in the most reasonable way in order to account for the great thickness of limestone, whose unrepeated thickness is known to be about 1,000 feet. Utilizing folds only, it requires a compressed sigmoid fold of limestone from whose anticline the quartzite has been pinched out and from whose syncline the slate. As against this a series of normal faults with southerly dip might be imagined but are less likely since the prevailing fault of this region is of the reversed type.

The lowest channel is almost beneath the present stream and stands at +10, somewhat unexpectedly high.

The Croton River.—From the Peekskill crossing the aqueduct bears away to the east and encounters so much high ground as to reveal little of moment from the depressions. But the earlier work in connection with the great dam across the Croton River gives us abundant data regarding this stream. Mica schist appears on the northwest bank and extends about half way across the valley. It is then succeeded by white marble to the south. The former would be interpreted by F. J. H. Merrill* as metamorphosed Hudson River slate; the latter as the recrystallized Wappinger. A possibly different view has been conservatively suggested by C. P. Berkey.†

SUMMARY OF TRIBUTARIES.

WEST BANK.

Name.	Distance from Hudson in miles.	Contour.
Esopus	25–30	+240
Esopus (Hurley)	13–18	— 68
Kripplebush	12–27	+ 80
Rondout	12	— 10
Wallkill. Spr. A.	12	— 79
" " B.	13	0
" L'lle	17	+ 65
Moodna	2	— 59

EAST BANK.

Name.	Distance from Hudson in miles.	Contour.
Casper	1/2	— 67
Wappinger	1/2	— 50
Fishkill	6	— 40
Sprout	3	— 8
Peekskill	3	+ 10
Croton	2	— 20

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* F. J. H. Merrill, The Geology of the Crystalline Rocks of Southeastern New York, 50th Ann. Rep. N. Y. State Museum; I. App. A. 21–31, 1898.

† C. P. Berkey, Structural and Stratigraphic Features of the Basal Gneisses of the Highlands, Bull. 107, N. Y. State Museum, 361, 1907.

The buried channel was found at −20, while the present Croton flowed at +50, leaving 70 ft. of drift, mostly of bowlder clay, between. The section is two miles from the Hudson.

Summary.—From this tabulation it is evident that considering the distances of the crossings from the Hudson, the Esopus at Hurley (or perhaps the Pliocene Kripplebush), and the Wallkill at Springtown A, have cut deepest. The bed-rock at their mouths must be relatively far down. For those near the river Casper Creek is strikingly low for a stream that is decidedly smaller to-day than the modern Wappinger. Fishkill Creek with −40 at six miles back may well be much deeper at its Pliocene mouth, but its location has not been established, much less explored. Even giving all possible latitude to these depths, it still remains true, that as compared with the gorge of the Hudson, now demonstrated at the Storm King crossing, all these tributaries entered in the last stages of erosion, either just preceding or during the Glacial epoch, by hanging valleys of 500 ft. or more above the bottom of the main stream.

The Hudson Crossings.

The borings which cross this great river furnish naturally the most interesting data of all, and, as will appear, they show a surprising depth to bed-rock. The crossings begin about eight miles north of Newburg or seven miles south of the Poughkeepsie bridge. They are somewhat irregularly distributed, but extend at the extreme limit, about two miles south of West Point. The one of greatest interest is the Storm King crossing, between Storm King mountain on the west and Breakneck mountain on the east. Of this we have the completest data, but there are core-borings available at Peggs Point, next to the most northerly crossing, and at Little Stony Point, although they are not numerous. All the rest are based on wash-borings, which, as already stated, are only of value in showing that the bed-rock is lower yet. In some of the wash-borings an artesian flow of fresh water was encountered which spurted above the decks of the lighters carrying the drills, deluging the drillers with water and sand. There is thus a connection with the hills on the banks and beneath the silt. A few little shells have been yielded from beds forty feet below the bottom of the river.

The Tuff Crossing.—This is situated a half-mile above Peggs Point, where the next crossing south was located, and runs diagonally across the river in a direction about N. 63 W. Its profile is shown in fig. 12. Hudson River slates are on the west bank, and the heavily bedded Wappinger limestone of the Clinton Point quarries on the east. The geological relations are presumably like those at Peggs Point, of which we have much fuller data. The wash-borings returned a fairly even profile for the supposed bed-rock, at depths varying from 210 to 236 below tide. Upon them, however, we can place no reliance.

The Peggs Point Crossing.—This is situated a half-mile south of the last named and strikes directly across the river at one of the narrowest possible passages. A steep hillside of Hudson River slate forms the west bank, while a short distance back from the east bank are the Clinton Point quarries in the Wappinger limestone. Several lines of wash-borings were run across, giving distances to supposed bed-rock ranging from 139·5 to 256 in what might be esteemed the depths of the river. The records were sufficiently discordant to induce the sinking of three diamond drill cores in the river and one on each bank, as shown in fig. 13. The deepest one caught the slate at 223 ft., a record not very different from some of the wash-borings. The next easterly one revealed the limestone at only 92 ft. There is an unexplored stretch of 1,040 ft. between, which presumably contains a deep and rather narrow gorge in order to fall in with the records of the Storm King crossing, roughly ten miles south. Otherwise the great depth at Storm King is very difficult to understand unless we assign to the river a fall of over 375 ft. in ten miles, certainly a most unusual gradient.

The borings on Casper Creek, which enters the Hudson just below this crossing, showed the bed-rock at -69, as has been already stated.

The New Hamburg Crossing.—Two miles south of Peggs Point the river narrows again between the point on which is situated New Hamburg on the east bank and Cedarcliff on the west. Only 2,300 feet intervene from shore to shore, but both banks have the Wappinger limestone. On account of an overthrust fault, which is beautifully shown near the north portal of the New Hamburg tunnel of the New York Central R.R. and is again revealed by the drill, we know that the slates lie beneath it as shown diagrammatically in fig. 14. Only wash-borings were made in the river bottom, but of these five different but closely adjacent lines were run, of which one typical case has been selected for the figure. Where taken beneath the portions of the river well out from the banks, the extremes were 130 and 263·5 with a general range from 195 to 255. Yet such wide differences were met as to destroy all confidence in the borings as indicative of the actual bed-rock. As against the maximum of 263·5 we may contrast the bed-rock in Wappinger Creek at 50 and less. Even this would indicate a hanging valley of over 200 feet, above the bottom of the Hudson.

Danskammer Crossing.—A mile south of New Hamburg, on the west bank, is a point with a lighthouse known as Danskammer, apparently from its having been a center of merry

FIG. 12.

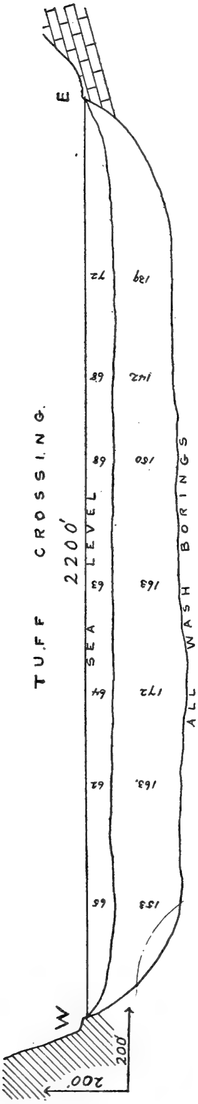

FIG. 13.

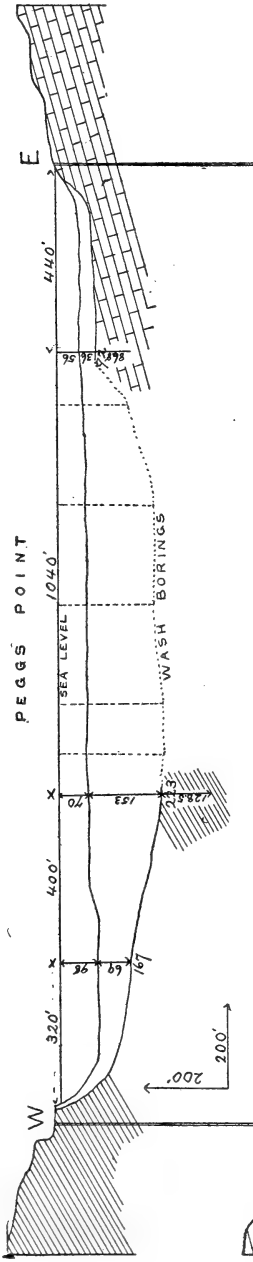

FIG. 14.

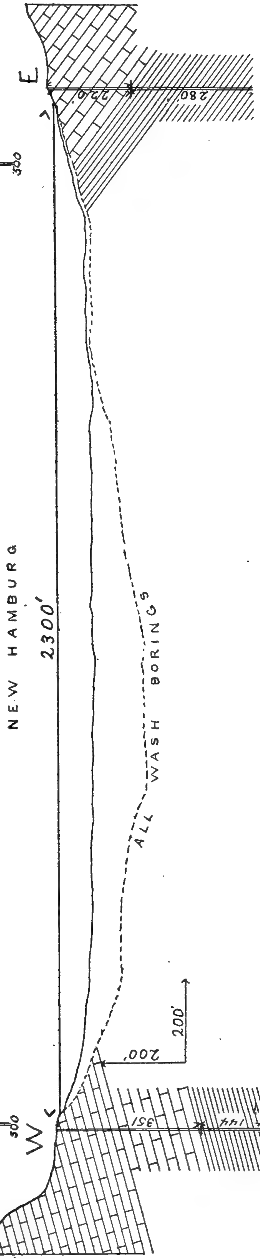

FIG. 12. The Tuff Crossing. FIG. 13. The Peggs Point Crossing. FIG. 14. The New Hamburg Crossing.

making in earlier years among the German-speaking inhabitants. The distance from bank to bank is 3,500 ft., and two lines of wash-borings were made. In the portions beyond the influence of the banks the depths range from a minimum of 133·2 to a maximum of 268·5, with a general range from 200 to 250. Again such wide variations were found and such irregularities as to only justify the inference of a bed of bowlders of irregular upper surface. The crossing passed from Wappinger limestone on the west bank to Hudson River slates on the east. The details are given in fig. 15.

The Storm King Crossing.—Some six miles south of Danskammer the abrupt ridge of the Highlands crosses the river, and Paleozoic strata give way to Archean granite. The river widens in Newburg bay, so that no more lines of borings were considered. Between the great granite buttresses of Storm King mountain on the west and Breakneck on the east it narrows to 2,800 ft., and at this point it was finally decided to locate the siphon for a number of important reasons, based upon the western approach and the local geology. Detailed exploration with the diamond drill was at once begun, but proved an exceedingly difficult matter to prosecute because of the bowlders which were encountered at two horizons. One is about two hundred feet from the surface and is thin; the other is roughly four hundred feet down and is thick and troublesome. The details are shown in fig. 16, in which the relations of a line of wash-borings to the actual bed-rock are brought out in an interesting manner. Besides the diamond drill-holes a shaft is being sunk on each bank for later use, as a part of the siphon, and for horizontal diamond drill-holes when sufficient depth is attained, to test the existence of fault-zones which vertical holes could not locate.

Hole 16 at 300 ft. from the east bank is certainly in the bed-rock at about 200 ft. Hole 19 at 560 ft. out probably stopped near it, but the tools met an almost impenetrable series of bowlders of large size and the hole was stopped. Hole 10 is not on the exact line of the others, but is 300 ft. nearly due south from No. 22. It is the most significant of all. It caught the rock at 608·6 ft., penetrated it for 8·8 ft., bringing up a core of granite identical with that on the banks. When this had been attained after months of difficult work, the tragedy of the crossing occurred. A river steamer, having passed the hole, suddenly became unmanageable from an accident, drifted down on the drill and caused the loss of the one hole which has as yet reached the bed-rock and, as we believe, penetrated it rather than a bowlder. It would indicate, therefore, the bottom at a depth of 608·8 feet.

FIG. 15.

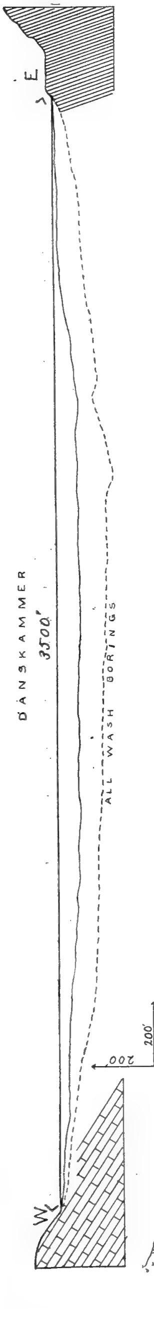

FIG. 16.

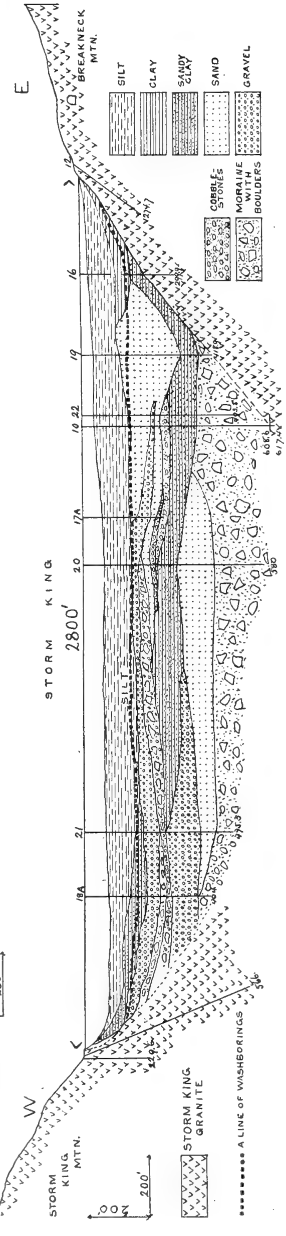

FIG. 17.

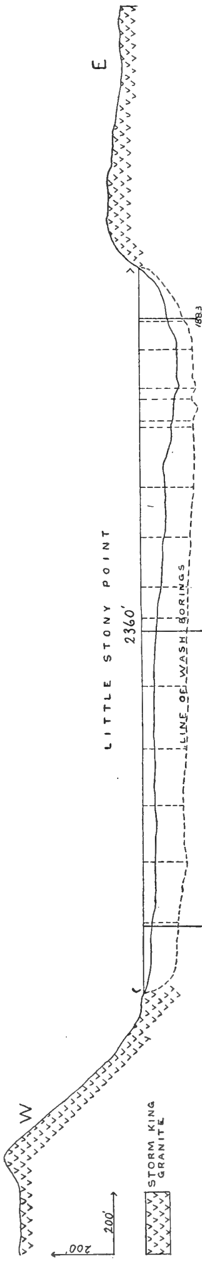

FIG. 18.

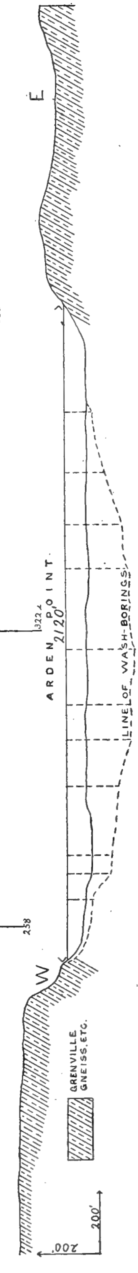

FIG. 15. The Danskammer Crossing. FIG. 16. The Storm King Crossing. FIG. 17. The Little Stony Point Crossing. FIG. 18. The Arden Point Crossing.

Hole 20 at 580 ft. failed to get through the bowlders, so that we only know that the bed-rock is still deeper. Hole 21, about 700 feet from the west bank, stopped in the bowlders at 475·3, so that we only know here that the bed-rock is deeper. It will be driven farther. Hole 18 at approximately 500 ft. from the bank was probably very near the bed-rock if not on it. The casing became bent and the hole was lost. The drillers believed that the bed-rock had been encountered at a shelving point so that the casing glanced off. This is not improbable, although a shelving bowlder is also a possibility.

If we believe that the great ice sheet found a V-shaped river valley in the Highlands and operated to change its section to the characteristic U-shape, then the bottom ought to flatten rapidly beyond hole 10, even if it had not already done so at this point. It is anticipated that future holes which are now being driven will find the bed-rock at depths not very much greater.

We are justified in inferring that on the retreat of the ice this gorge was left with some 200 ft. of bowlders and sand on its bottom. Upon this foundation subsequent water deposited about 200 ft. of sand, gravel, and sandy clay. Either a slight readvance of the ice sheet or floating ice then yielded the upper, thin bowlder bed, after which only fluviatile conditions prevailed. If we do not credit the great glacier with much eroding power, then the continent must have been elevated decidedly over 600 ft. in order to provide a run-off. But if we believe that the ice-sheet operated to deepen this channel, then this amount of elevation is not absolutely necessary. The heavy, bottom bowlder-bed indicates that after the retreat of the ice fluviatile scour has not affected the bed-rock.

The Little Stony Point Crossing.—About a mile south of Storm King a point juts out from the east bank called Little Stony. The river narrows to 2,360 ft., and a line of wash-borings was made with the results shown in fig. 17. No one of them reached 200 ft. Three diamond drill-holes were also sunk, of which the deepest, near the middle of the river, reached 322·2 ft. They all stopped in bowlders, so that to this extent the deep gorge is corroborated.

The Arden Point Crossing.—Three or four miles south of the Little Stony crossing and about a mile below West Point is the Arden Point line, to which some exploration has been directed. The shores are in the sedimentary metamorphics of the Highlands, and on fig. 18 are called Grenville, using the name current in the Adirondacks and Canada. The river is only 2,120 ft. wide, so that the shortest section beneath its water of all those tested is afforded. Wash-borings, the only ones used, reached depths of 220 ft. and less. The line, however, was abandoned for other reasons before any core-borings seemed called for.

Concluding Remarks.—The great depth to bed-rock at the Storm King crossing leads to some interesting lines of reflection. We have no reason to think that the river has ever done otherwise than flow down-grade to the sea along its present channel. Some suggestions have been made of its diversion to the Hackensack valley, but in this the writer and his colleague, Dr. Berkey, who is very familiar with the local geology, have no confidence whatever. For this region we believe in a rather abrupt elevation of the land in the closing Tertiary which brought about a deepening of stream channels to a point as much below the present as the depths of the exploring holes, above cited, indicate. The Hudson, however, obviously cut much more rapidly than its tributaries, and with this the temporary diversion of the drainage of the Great Lakes through the Mohawk may have had some influence. The ice-sheet served to still further accentuate the difference, and, as often appears along a trunk glacier, left the tributaries as hanging valleys. The drill-holes at Peggs Point prove that at this crossing the gorge must be relatively narrow, but since there seems no way of explaining the depths at Storm King by a gigantic pothole or exceptionally deep, local scour, or any other reasonable method other than water or ice erosion, the still undiscovered gorge is inferred in the 1,040 ft. between the holes. Since the Storm King granite is the hardest and most resistant rock in the whole course of the river, if it has yielded anything unusual it ought to form a reef rather than a depression.

Doubtless the thought will come to a reader, as to the character of the Hudson valley opposite New York. Thus far only the records of wash-borings have been published, and of these the deepest is 300 ft. at a point 2,000 ft. off the bulkhead at 57th street.* Yet there is reason to anticipate something like 700 ft. or more to bed-rock, and the hope may be expressed that some future exploration for an engineering enterprise will give the actual determinations.

Postscript.—Since July 15, when the above pages were completed, additional data have been obtained at the Storm King Crossing as follows (compare fig. 16): Hole 22 has caught the granite at 507′, indicating that the profile of the eastern bottom flattens from hole 19 to this point, more than as sketched. Hole 20 is 626′ and is in fine sand and clay. Hole 21 had penetrated 4 to 5 feet in a granite ledge or bowlder when temporarily stopped by the collision of a tow. Thus the extreme depth has not yet been reached and appears to be beneath the middle of the river near Hole 20.

August 31, 1908.

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* Cited by W. H. Hobbs in U. S. Geol. Survey Bulletin 270, p. 31, from Ch. McDonald, Engineering News, xxxiii, 159, 1895.

ART. XXXV.—*Thomson's Constant, e, Found in Terms of the Decay Constant of Ions, within the Fog Chamber;* by CARL BARUS.

1. *Introductory.*—In the last paper,* an account is given of certain tentative experiments to determine Thomson's electron, by aid of the fog chamber and a separate well-leaded cylindrical electrical condenser. The results obtained for *e* agreed well with the accepted values. It was shown that the constants of coronas are determinable from purely optical consideration of diffraction and interference, and that the accuracy of the method may be enhanced by using the mercury lamp as a source of light for the coronas. There was, however, one grave misgiving; inasmuch as the distribution of ionization within the fog chamber varies in marked degree from place to place, for any given position of a sealed radium tube, and that the mean value assumed was in a measure gratuitous. The results seen in the fog chamber are a complication of the effects of primary and secondary radiations together with a very marked exhaustion displacement of the ions. The maximum ionization does not coincide, as a rule, with the position of the radium, and there is no reason why the ionization in the fog chamber should be quite identical with the ionization produced by the same radium tube in the electrical condenser, unless both are one in the same apparatus. This is the case in the experiments of the present paper.

2. *Electrical condenser—fog chamber.*—It is therefore necessary to make the fog chamber itself an electrical condenser, and this is easily done if the chamber is cylindrical, by installing a tubular core of aluminum closed in the inside of the chamber and running axially from end to end. This core is charged to a definite potential and made the inner surface of the condenser, while the scrupulously clean inner wall of the glass chamber (to which water adheres easily) is the outer surface and put to earth. Finally the radium, contained in small sealed tubelets of aluminum, is placed within the length of the axial aluminum tube or core, in such a way as to make the ionization within the fog chamber uniform,—a condition vouched for in case of the occurrence of uniform coronas on exhaustion, from end to end of the chamber.

There are thus three currents to be determined. (1) The conduction current due to inevitable leakage between the condenser surfaces. This is made a minimum and nearly negligible in value, by keeping the aluminum core out of the

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* C. Barus: This Jour., xxvi, pp. 87–90, 1908.

condenser except when not in use and by sheathing it with an annular air space beyond the condenser. It is found experimentally, by direct measurement in the absence of radium. (2) The current resulting from the ionization of the room air near the fog chamber and on the outside of it, due to gamma rays. This is made a minimum by allowing the thin wire communicating with the electrometer to run axially away from the fog chamber; for the gamma rays, in spite of their penetrating power, are quickly reduced by distance. This current is found in the presence of radium within the axial tube, by leaving all adjustments identically in place, but breaking the metallic connection between the aluminum core and the electroscope, etc., by a hard rubber insulator. If an auxiliary condenser is used, the measurement (1) must be made without it, as otherwise its leak would be counted twice. Fortunately the conduction current is relatively quite negligible. (3) The current due to ionization within the fog chamber. This is found by deducting from the total current found on connecting the charged aluminum core and the electrometer, the two preceding currents.

3. *Auxiliary condenser.*—To vary the experiments to the extent that different speeds of leakage may be obtained, as well as to find the capacities of the electrometer and fog chamber, an auxiliary condenser must be inserted as a part of the electroscope. This condenser consisted in the present experiments of two plates of brass, having an area of $315^{\text{sq cm}}$, and usually kept at a distance of $\cdot 32^{\text{cm}}$ apart by outrigged feet of hard rubber, which stood on a plate of glass. By putting small glass plates under these feet, this capacity could be varied at pleasure. The usual equation was corrected by aid of the factor

$$1 + (d + d\,ln\,16\sqrt{a\pi}\,(d+\theta)/d^2 + \theta\,ln\,(d+\theta)/\theta)/\sqrt{a\pi},$$

where a is the area, d the distance apart and θ the thickness of the plate of the auxiliary condenser. Naturally a guard ring condenser would have been preferable for standardization, but none was at hand.

To determine the very small capacity C of the electroscope-fog-chamber, two successive full charges from the lighting circuit, at a potential $V = 250$ volts, were in turn imparted from C to the auxiliary of capacity C'. If V'' be the potential observed after these two charges and $S = V''/(V - V'')$, $C = C'S/(1 + \sqrt{1+S})$. It is curious that this method of successive charges leads to complicated cubic, quartic, quintic equations, etc., which follow no simple rule. The ratios R of the potentials after four and after two charges $R = V''''/V''$ is however still available. Apart from these complications, the large deflections obtainable after many successive charges would, in the absence of conduction leakage in the condensers, make this method very satisfactory.

In the definite measurements, however, almost the whole capacity may be placed in the auxiliary condenser, so that the capacities of the electrometer and fog chamber are of small importance. Ratios of $C'/C = 86/17, 30/17, 20/17$, and others, were tried.

4. *Method.*—In the preceding paper the value of e found was ultimately dependent upon the velocity of the ions in the unit electric field. In the present experiments a value will be investigated, based on the decay constant $b = 1{\cdot}1 \times 10^{-6}$, of the ions. This method has the advantage that large core potentials are admissible in the electrical condenser, so that an ordinary graduated Exner electroscope suffices for the measurement of current. The small capacities of the instrument make it necessary to insert an auxiliary condenser, as otherwise the discharges are too rapid for trustworthiness.

If a is the number of ions produced per second per cubic centimeter by the radium placed within the condenser core, and N the number of nuclei (ions) found when the core is free from charge, $dn/dt = a - bN^2 = 0$. Again if n is the number of nuclei found when the core is charged and i the corrected current observed, e Thomson's constant and v the effective volume of the fog-chamber-condenser, $dn/dt = b(N^2 - n^2) - i/ev = 0$. Hence if the capacity of the system is C and $\dot{V}$ the corrected fall of potential per second

$$e = C\dot{V}/(bv(N^2 - n^2))$$

Usually $\dot{V}$ is measured in volts, so that $\dot{V}/300$ replaces $\dot{V}$ in the equation. It is obvious that V must be large enough to keep the current $\dot{V}$ constant, and the observations always show this at once.

5. *Data disregarding external gamma rays.*—The aluminum foil electroscope made it convenient to use the high potentials of the electric lighting circuit (about 250 volts) for charging.

The number of nuclei (ions) found in the *exhausted* fog chamber free from charge, at its central core, was $N = 474{,}000$. The number of nuclei found in the exhausted fog chamber when the core was charged to 250 volts was $n^1 = 82{,}500$. Hence about 391,000 vanished in the presence of the electrical current, the original apertures of the coronas being reduced from about 22 degrees to 13 degrees. The drop of pressure $\delta p/p = {\cdot}30$ nearly, was taken high enough to catch all the ions, but not so high as to catch the vapor nuclei of dust-free wet air.

The amount of exhaustion was equivalent to the volume ratio $v_1/v=1{\cdot}29$. Thus the number of ions in the fog chamber at atmospheric pressure was $N=611{,}000$ per cubic centimeter for the uncharged core and $n=106{,}000$ for the charged core. Hence N^2-n^2 is about 362×10^9.

The value of $b=1{\cdot}1\times10^6$ is taken from Prof. Rutherford's book. The source of light for the corona is part of a Welsbach mantle, as usual, and the old constants of coronas were used, since it is a part of the purpose of this paper to test those constants. The volume of the fog chamber was estimated at 51,000 $^{\text{cu cm}}$. In the first experiments, the effect of the gamma rays penetrating into the air on the outside of the fog chamber was *neglected* and the data on using different condensers were as follows, all data being given in electrostatic units. C denotes the capacity of the system, $\dot{V}$ the drop of potential per second, i the corrected current passing through the condenser fog chamber.

C	$\dot{V}\times10^3$	$i\times10^2$	$e\times10^{10}$
103	10	103	5·1
47	21	101	5·0
47	19	92	4·5
17	40	70	3·4

the last observation being made without an auxiliary condenser. The current i was quite constant throughout the voltage interval (near 250 volts) of observation. Hence the effect of gamma ray penetration has seriously increased the leakage, and e therefore appears too large, except in the last observation, where i is probably no longer measureable.

6. *Further data.*—In the following experiments the effect of the external gamma rays was eliminated as specified in § 2. The conduction current was usually quite negligible. The nucleations observed in the exhausted fog chamber were $n=82{,}000$ and $N^1=506{,}000$, when the core was charged and uncharged, respectively. The exhaustion was again equivalent to a volume increase of $v_1/v=1{\cdot}29$. Hence in the fog chamber full of air the respective nucleations are $N=653{,}000$ and $n=106{,}000$, whence $N^2-n^2=415\times10^9$.

The electrical measurements, if all data are given in electrostatic units, may be summarized as follows:

C	$\dot{V}\times10^3$	$i\times10^2$	$e\times10^{10}$
103	7·5	77	3·3
47	17·2	81	3·5
37	19·6	72	3·1
17	33·	58	2·5

Thus with a correction for the external gamma radiation, the data for e show reasonable values, in spite of the simplicity of the experiment. It follows, therefore, that even in the case of such large numbers of ions as occur in these experiments (over 500,000), both positive and negative ions must have been caught in the fog chamber and that the constants of coronas used heretofore are substantially correct. In case of the last value $e\times 10^{10}=2\cdot 5$, for the small capacities of 17^{cm}, the aluminum leaves on the electroscope converge too rapidly for measurement, so that the air resistance may have produced an appreciable discrepancy. Hence both i and e are too small. No refinement has been attempted in these experiments, their chief purpose being to test the standardization of the fog chamber in terms of coronas and the degree to which positive and negative ions may be caught even at very high nucleation. One may note in conclusion that the currents of the order of $i=77$ electrostatic units or $2\cdot 6\times 10^{10}$ amperes, are already quite within the reach of the sensitive galvanometer.

My thanks are due to Miss L. B. Joslin, for assistance throughout this investigation.

Brown University, Providence, R. I.

Art. XXXVI.—*The Application of the Cobalti-Nitrite Method to the Estimation of Potassium in Soils*; by W. A. Drushel.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cxc.]

In a previous paper* from this laboratory it was shown that potassium may be estimated with a fair degree of accuracy by precipitating it as potassium sodium cobalti-nitrite in a solution acidified with acetic acid and oxidizing the precipitate with standard potassium permanganate. In the same paper the applicability of the method to the estimation of potassium in commercial fertilizers was shown by a series of experiments.

In the method as previously worked out an excess of concentrated sodium cobalti-nitrite solution acidified with acetic acid is added to a neutral solution of a potassium salt, and the mixture is evaporated to a pasty condition on the steam bath. After cooling, the residue is stirred up with sufficient cold water to dissolve the excess of sodium cobalti-nitrite. The precipitate, consisting of $K_2NaCo(NO_2)_6.H_2O$, is filtered on a rather close asbestos felt in a perforated crucible and well washed with cold water, or preferably with a half saturated sodium chloride solution. The precipitate and felt are transferred to an excess of standard N/10 or N/5 potassium permanganate which has been diluted to about ten times its volume and heated nearly to boiling. If particles of the precipitate stick persistently to the walls of the crucible and cannot be removed with a spray of water, the crucible is put into the permanganate solution. After stirring for a few minutes the solution is gradually acidified with 5^{cm^3} to 20^{cm^3} of dilute sulphuric acid, and the oxidation is allowed to go to completion, a process which seldom requires more than five minutes. If no particles of the yellow precipitate settle out on standing a minute, the oxidation may be considered complete. The hot solution is then bleached by running in a measured amount of standard oxalic acid, containing 50^{cm^3} of concentrated sulphuric acid per liter. The solution after bleaching is titrated to color with standard permanganate in the usual manner.

In this process the cobalt in the molecule is reduced from the trivalent to the bivalent condition and not reoxidized, consequently from the molecule of the potassium sodium cobalti-nitrite we find 0·000857 grm. K_2O equivalent to 1^{cm^3} of strictly N/10 potassium permanganate. This factor of course must be corrected for any variation in the normality of the permanganate solution used.

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* This Journal, xxiv, 433, 1907.

For the extraction of the alkalis 10 grm. of dry soil are placed in an Erlenmeyer flask with 25^{cm^3} to 35^{cm^3} of about 20 per cent. hydrochloric acid. The flask is thoroughly shaken and a small funnel is hung in its neck to avoid too great a loss of acid by evaporation. The contents of the flask are digested on the steam bath for 24 hours.

From this point several methods for the final preparation of the sample were tried with satisfactory results, given in the table. Since duplicate estimations were to be made by the gravimetric chlorplatinate method, for which it was necessary to remove the iron, aluminum, calcium, magnesium, phosphoric acid and ammonium salts, if present, from the soil extract, the following general procedure was found to be most expeditious. The soil extract was filtered through paper into an evaporating dish and the residue was washed with boiling water until the filtrate gave no reaction for chlorine with silver nitrate. The filtrate was evaporated almost to dryness to remove the excess of hydrochloric acid as far as possible. The residue was dissolved in about 200^{cm^3} of water and, after heating to boiling, a little ammonium hydroxide and ammonium oxalate were added. The mixture was boiled a minute, settled, filtered and the precipitate was washed with hot water until a drop of the filtrate give no chlorine reaction. The filtrate was concentrated, transferred to a 200^{cm^3} flask, cooled, and made up to the mark. After thoroughly shaking, 50^{cm^3} aliquots were pipetted off for the gravimetric and volumetric estimations. The aliquots were evaporated to dryness in platinum dishes, and gently ignited to remove the ammonium chloride. After cooling, the residue was moistened with dilute sulphuric acid and again ignited, gently at first and finally at the full heat of the Bunsen flame, to remove the last trace of ammonium present as the sulphate, and to destroy any organic matter which might be present.

The residue for the gravimetric estimation was dissolved in a little water and a few drops of hydrochloric acid over the steam bath, and the estimation of the potassium was made according to the modified Lindo-Gladding method.

To dissolve the residues for the volumetric estimations a little water and a few drops of acetic acid instead of hydrochloric acid were used. In the volumetric work approximately N/5 potassium permanganate was used, $26{\cdot}08^{cm^3}$ of permanganate being equivalent to 50^{cm^3} of exactly N/10 oxalic acid. From this ratio the factor for K_2O was found to be 0·001642. In each case the potassium was precipitated as the cobalti-nitrite by evaporating off with 10^{cm^3} of sodium cobalti-nitrite prepared according to the method of Adie and Wood.*

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* Journ. Chem. Soc., lxxvii, 1076–80 (London).

No.	Character of soil		Soil taken grm.	Method	K_2O found grm.	per cent.
I	Clay	(1)	2·5	vol.	0·0028	0·11
		(2)	"	"	0·0035	0·14
		(3)	"	grav.	0·0035	0·14
II	Clay	(1)	"	v.	0·0100	0·39
		(2)	"	"	0·0092	0·37
		(3)	"	g.	0·0093	0·37
III	Loam	(1)	"	v.	0·0074	0·30
		(2)	"	"	0·0068	0·27
		(3)	"	g.	0·0075	0·30
IV	Loam	(1)	"	v.	0·0060	0·24
		(2)	"	"	0·0058	0·23
		(3)	"	g.	0·0058	0·23
V	Gravel	(1)	"	v.	0·0042	0·17
		(2)	"	g.	0·0045	0·18
VI	Gravel	(1)	"	v.	0·0047	0·19
		(2)	"	"	0·0044	0·18
		(3)	"	g.	0·0050	0·20
VII	Clay Gravel	(1)	"	v.	0·0048	0·19
		(2)	"	g.	0·0046	0·18
		(3)	"	v.	0·0045	0·18
		(4)	"	"	0·0040	0·16
		(5)	"	"	0·0044	0·18

The following exceptions are to be noted to the general method previously outlined for the preparation of the sample. In I the excess of hydrochloric acid, the iron, aluminum and calcium were removed from the separate portions after aliquoting, and in (1) and (2) sodium carbonate was used instead of ammonium hydroxide and ammonium oxalate for the removal of the iron, aluminum and calcium. In V (1) and (2) bases other than the alkalis were removed in the separate aliquots by ammonium hydroxide and ammonium oxalate. In VII the aliquots were made directly from the hydrochloric acid extract. That of VII (2) was treated in the usual manner for the gravimetric estimation of potassium. The other aliquots of VII were evaporated to dryness and gently ignited to remove any ammonium chloride present and to char the organic matter. The residues were extracted with hot water and a little acetic acid, filtered and evaporated with sodium cobalti-nitrite in the usual manner.

In this work the results are based on a small amount of soil (2·5 grm.) in each case because but a limited amount of each sample was available. A higher degree of accuracy may be secured by using 10 grm. of soil for each estimation instead of 2·5 grm.

Summary.

A weighed amount of dry soil is extracted with an excess of hydrochloric acid over the steam bath. The excess of acid is removed from the extract by evaporation. The bases which might interfere with the process are removed with sodium carbonate or ammonium hydroxide and ammonium oxalate. Ammonium salts and organic matter are removed by ignition. The residue is dissolved in a little water and a few drops of acetic acid, and the mixture evaporated with an excess of sodium cobalti-nitrite to a pasty condition, stirred up with cold water, and filtered upon asbestos in a perforated crucible. The precipitated potassium sodium cobalti-nitrite is washed with half-saturated solution of chloride, and treated with an excess of permanganate in hot dilute solution. The color of the permanganate is destroyed by an excess of standard acidulated oxalic acid, and the excess of oxalic acid titrated to color with permanganate.

Art. XXXVII.—*The Iodometric Estimation of Chromic and Vanadic Acids in the Presence of One Another;* by Graham Edgar.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cxci.]

The difficulties which are met in the separation and gravimetric estimation of chromium and vanadium have led to various attempts to accomplish the estimation of these elements in the presence of one another. In 1898 Hillebrand* proposed a method based on the fact that chromium may be accurately estimated when present in small quantities by comparison of the color of the solution containing an alkali chromate with that of standard solutions of potassium monochromate. If then the solution be reduced with sulphur dioxide and the excess removed by boiling, vanadium, if present, may be estimated by titration with standard potassium permanganate. This latter process, however, is open to the objection that if titration be made in the hot solution an appreciable amount of chromic salt is oxidized, while if the solution be cold the end point is more or less uncertain. If, however, a correction be made for the permanganate used up in partially oxidizing the chromium, the method is accurate for the small quantities of vanadium found in rocks.

A method has been also proposed by Campagne† for the estimation of these elements in the same solution, in which the vanadium is estimated by titration with potassium permanganate after reduction with hydrochloric acid and subsequent treatment with concentrated sulphuric acid to convert the oxychloride into oxysulphate. The solution is then boiled with an excess of strong potassium permanganate, the excess of reagent destroyed by the addition of a piece of filter paper, and the oxides of manganese filtered off, the filtrate containing the vanadium as vanadate and the chromium as chromate. Ferrous ammonium sulphate in excess is now added and this excess determined by titration with potassium permanganate, the difference being of course the amount of ferrous salt used up in reducing the chromic acid, thus allowing the chromium to be calculated.

The definiteness with which vanadic acid is reduced to different stages of oxidation by means of varied reducing agents makes it especially suited for processes of differential reduction, in which the substance to be analyzed is treated with two or more reducing agents whose action upon the constituents to be estimated is different. The latter are then calculated from the determination of the total reducing effect in each case.

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* Journal Amer. Chem. Soc., 20, 461–465.

† Bull. Soc. Chim. (3), xxxi, 962–965.

That vanadic acid is reduced under proper conditions to the state of tetroxide by hydrobromic acid has been shown by Holvescheit,* and that the reduction may be carried to the state of trioxide by hydriodic acid has been shown by Friedham and Euler,† by Gooch and Curtis,‡ and by Steffan.§ Chromic acid, however, is reduced to a chromic salt by both hydrobromic‖ and hydriodic acid. In 1895, Friedheim and Euler¶, in connection with their work upon the estimation of vanadic and molybdic acids, suggested that vanadic and chromic acids might be estimated in the presence of one another by a process based upon the differential reducing action of hydrobromic and hydriodic acid: but inasmuch as no experimental data were given and as none have appeared on the subject in the thirteen years now elapsed, the present writer has considered himself justified in investigating the feasibility of such a process.

The apparatus used will be briefly described. As reduction flask served a 100^{cm^3} Voit flask, to the inlet tube of which was sealed a small separatory funnel, serving for admission of acid to the flask and for the entrance of a current of pure hydrogen gas from a Kipp generator. To the outlet tube of the Voit was sealed a Drexel bottle, provided with a Will and Varrentrap trap, the two serving as absorption apparatus for the bromine and iodine liberated in the process.

The experiments were carried out as follows: Portions of standard solutions of sodium vanadate and potassium bichromate were measured into the Voit flask, one to two grams of potassium bromide were added, and the flask connected with the absorption apparatus containing a solution of potassium iodide made alkaline with sodium carbonate or sodium hydroxide, and the whole apparatus filled with hydrogen gas. Fifteen to twenty cubic centimeters of concentrated hydrochloric acid were added through the separatory funnel and the solution boiled for ten minutes, the reduction having been found to be always complete in that time. A slow current of hydrogen was maintained to avoid the "sucking back" of the liquid from the Drexel bottle. The apparatus was disconnected, the Voit flask placed in a beaker, containing cold water, and the alkaline solution in the absorption apparatus cooled by running water. The contents of the trap were washed into the Drexel bottle and the solution therein made slightly acid with hydrochloric acid. The liberated iodine was titrated with approximately N/10 sodium thiosulphate and the color brought back by a drop or two of N/10 iodine solution, after the addition of starch. The results of this titration are given in the following table:

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* Inaug. Diss. Berlin, 1890.

† Ber. Dtsch. Chem. Ges., xxviii, 2067–2073.

‡ This Journal, ii, 156–162.

§ Treadwell, Quantitative Analysis, p. 327.

‖ Farsöe, Zeitschr. Anal. Chemie., 1907, 308–310.

¶ Loc. cit.

No. of Expt.	V_2O_5 taken as $NaVO_3$ grm.	CrO_3 taken as $K_2Cr_2O_7$ grm.	(I) $Na_2S_2O_3$ N/10 × 1·031 cm³	(II) $Na_2S_2O_3$ N/10 × 1·031 cm³	Error on V_2O_5 grm.	Error on CrO_3 grm.
(1)	0·1523	----	16.20	16·22	(I) ±0·0000 (II) +0·0002	----
(2)	0·1523	----	16·19	16·20	(I) −0·0001 (II) ±0·0000	----
(3)	0·2031	----	21·59	21·58	(I) −0·0001 (II) −0·0002	----
(4)	0·1523	0·0685	36·08	16·22	+0·0002	−0·0001
(5)	0·1523	0·0685	36·10	16·20	±0·0000	±0·0000
(6)	0·1523	0·0085	36·12	16·17	−0·0003	+0·0002
(7)	0·1523	0·0685	36·07	16·20	±0·0000	−0·0001
(8)	0·1523	0·1370	56·00	16·17	−0·0003	+0·0001
(9)	0·1523	0·1370	56·02	16·22	+0·0002	±0·0000
(10)	0·1523	0·1370	56·03	16·19	−0·0001	+0·0001
			N/10 × 0·992	N/10 × 0·992 —	Changed Stand. of $Na_2S_2O_3$	
(11)	0·2031	0·1370	63·82	22·46	±0·0000	−0·0001
(12)	0·2031	0·1370	63·80	22·48	+0·0002	−0·0003
(13)	0·1016	0·0685	32·00	11·25	+0·0002	+0·0001
(14)	0·1016	0·0685	31·92	11·24	+0·0001	−0·0001
(15)	0·1016	0·0685	31·90	11·25	+0·0002	−0·0002
(16)	0·0508	0·0343	15·95	5·63	+0·0002	−0·0001
(17)	0·0508	0·0343	15·95	5·62	+0·0001	−0·0001

Alkaline potassium iodide was again placed in the absorption apparatus and the latter connected with the Voit flask. The current of hydrogen was turned on and, after all air had been expelled, the apparatus was disconnected momentarily, one or two grams of potassium iodide were added to the solution in the Voit flask, and connections made again. Through the separatory funnel ten to fifteen cubic centimeters of concentrated hydrochloric acid and three cubic centimeters of syrupy phosphoric acid were added and the solution in the reduction flask was boiled to a volume of ten to twelve cubic centimeters. The absorption apparatus was removed and cooled, hydrochloric acid was added and the liberated iodine titrated with approximately N/10 sodium thiosulphate. The results of this titration are given under II, Table I. It is evident that the iodine determined in the first titration corresponds to reduction of the chromic and vanadic acids corresponding to the equation,

$$V_2O_5 + 2CrO_3 + 8HBr = V_2O_4 + Cr_2O_3 + 8I + 4H_2O$$

while in the second case the iodine corresponds to a reduction of the vanadium tetroxide to trioxide as indicated in the equation,

$$V_2O_4 + 2HI = V_2O_3 + 2I + H_2O$$

The second titration, therefore, determines the vanadic acid present, and the difference between the first and second furnishes the necessary data for the calculation of the chromium.

From the small error shown in the results of Table I it is evident that vanadic and chromic acids may be accurately estimated in the presence of one another by the differential reducing action of hydrobromic and hydriodic acids under the conditions used above, the liberated halogen being absorbed in potassium iodide solution and the iodine titrated with sodium thiosulphate.

ART. XXXVIII.—*An Apatitic Minette from Northeastern Washington*;* by FREDERICK LESLIE RANSOME.

IN the course of a rapid reconnaissance along the Northwest Boundary in the summer of 1901, numerous dark micaceous dikes were noted on both sides of the Columbia River, between the smelter-town of Northport, Wash., and the settlement of Waneta, at the mouth of Pend d'Oreille River, in British Columbia. These dikes cut a series of sediments of unknown age, possibly Carboniferous, consisting of steeply inclined dark slates, banded schistose limestones, and subordinate quartzites. Similar dikes were noticed for 12 miles eastward along the Pend d'Oreille and as far west as Kettle River, which crosses the boundary about 40 miles from Waneta. Not all of these dikes have been carefully studied, but most of them appear to be minettes or rocks closely related to this type. One specimen from a particularly micaceous dike at the mouth of Sheep Creek, on the northwest bank of the Columbia opposite Northport, has been analyzed by Dr. W. F. Hillebrand and found to be of rather unusual chemical character—enough so, it is thought, to warrant the publication of the analysis with a petrographical description.

The rock is dark, greenish gray, by far the most prominent constituent in hand specimens being the closely crowded scales of biotite up to 4 or 5 millimeters in diameter. The other mineral constituents form in general a fine-grained matrix to the biotite and are not individually distinguishable without a lens. Parts of the rock, however, contain irregular light-colored streaks in which the feldspar is a little more distinct than elsewhere.

Under the microscope the rock shows a poikilitic texture, large irregular areas of optically continuous feldspar being crowded with automorphic crystals of biotite, pyroxene, apatite and titanite. The feldspar is chiefly orthoclase, although much of it is not optically homogeneous and some evidently contains microperthitically intergrown albite. It is all more or less turbid with minute, brown, dust-like inclusions. The biotite is chestnut-brown in most sections with the usual strong absorption parallel with the cleavage. The axial angle is small and the interference figure shows no distinct opening of the lemniscate cross into hyperbolas. The pyroxene, which is automorphic in the prism zone with occasional terminal planes, is monoclinic with a maximum observed extinction of $Z \wedge c$ of about 45°. It is colorless to very pale green, non-pleochroic and is probably an augite near diopside in compo-

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sition. The pyroxene is for the most part fresh, but some crystals have undergone slight partial alteration into green hornblende and calcite. The apatite occurs in stout prisms up to two millimeters in length and is noticeably abundant as seen in thin sections. It is included chiefly in the orthoclase and biotite, although the augite is not free from occasional prisms. Rather abundant titanite and a little magnetite and pyrite make up the minor constituents.

The chemical analysis of this rock by Dr. Hillebrand is as follows:

Chemical Analysis of Minette.

SiO_2	41·57	F	·23
Al_2O_3	9·75	Cr_2O_3	·04
Fe_2O_3	4·06[*]	NiO	·02
FeO	4·47[*]	MnO	·25
MgO	8·65	BaO	·44
CaO	11·10	SrO	·11
Na_2O	1·57	Li_2O	trace
K_2O	6·10	V_2O_3	·04
H_2O-	1·54	FeS_2	·06
H_2O+	2·30		
TiO_2	2·36		100·01
ZrO_2	·02	Less O for Fl, Cl,	·11
CO_2	1·24		
P_2O_5	4·05		99·90
Cl	·04		

In comparison with most minettes the analysis of the rock here described is low in silica and alumina, rather high in potash and titania, and remarkably high in phosphoric acid. This last feature, indeed, is the most noteworthy peculiarity of the rock. Out of the 2112 rocks of which superior analyses are collected in Washington's tables[†] only 59, or 2·7 per cent, contain over 1 per cent of P_2O_5. Of these only 10 contain over 2 per cent, and, of these 10, only 2 have over 3 per cent of P_2O_5, namely a pyroxene-apatite-syenite (orendase) from Finland, described by Hackman,[‡] with 5·98 per cent of P_2O_5 and an avezacite (avezaciase) from the Pyrenees described by Lacroix[§] with 3·32 per cent of P_2O_5.

The norm as calculated from the chemical analysis and the place of the rock in the quantitative classification are as follows:

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[*] Not corrected for influence of V_2O_3.

[†] Washington, H. S. Chemical analyses of igneous rocks. Professional Paper U. S. Geol. Survey No. 14, 1903; Superior analyses of igneous rocks. Professional Paper U. S. Geol. Survey No. 28, 1904.

[‡] Hackman, V. Neue Mittheilungen über das Ijolithmassiv in Kuusamo. Bull. commission Géologique de Finlande No. 11, 1899, pp. 36–37.

[§] Lacroix, A. Les roches basiques accompagnant les lherzolites et les ophites des Pyrénées. Comte Rendu VIII Congrès Géol. Int. 1900, Paris, 1901, p. 382.

Norm.		
Or	28·91	
Ne	7·10	
Lc	5·67	Sal.=43·07
An	1·39	
Di	22·38	
Ap	9·41	Fem.=51·11
Ol	8·73	
Mt	6·03	
Il	4·56	
H_2O	3·84	
CO_2	1·24	
FeS_2	·06	
	99·32	

$$\frac{\text{Sal.}}{\text{Fem.}}=\frac{43{\cdot}07}{51{\cdot}11}=\text{III, Salfemane.}$$

$$\frac{\text{L}}{\text{F}}=\frac{12{\cdot}77}{30{\cdot}30}=6,\ \text{Portugare.}$$

$$\frac{K_2O+Na_2O}{CaO}=\frac{90}{5}=1.\quad \text{Wyomingase.}$$

$$\frac{K_2O}{Na_2O}=\frac{65}{25}=2.\quad \text{Washingtonose.}$$

This norm, as shown above, places the rock in the salfemane class, in the lendofelic or Portugare order, in the peralkalic or Wyomingase rang, and in the dopotassic subrang. It is the first recorded representative of this subrang, and as it falls well within the classificatory limits of the division, *washingtonose* is suggested as an appropriate subrang name. It is worthy of note that the wyomingite, orendite and madupite described by Cross* from the Leucite Hills, Wyoming, are all comparatively rich (1·39 to 1·89 per cent) in phosphoric acid.

For comparison the norms of the two rocks standing nearest to washingtonose in Washington's tables† are given below.

Wyomingite (*Cross*).

Or	44·5
Lc	10·5
Ne	1·7
Ac	7·4
Di	13·9
Ol	7·9
Il	4·1
Hm	0·8
Ap	4·5

Shonkinite (*Weed and Pirsson*).

Or	29·5
Ab	8·9
An	1·1
Ne	6·2
Di	28·9
Ol	14·8
Mt	5·1
Il	1·4
Ap	1·7

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* Cross, W. Igneous Rocks of the Leucite Hills and Pilot Butte, Wyo., this Journal (4), vol. iv, p. 130, 1897.

† Professional Paper U. S. Geol. Survey No. 14, p. 339.

The wyomingite is in the perpotassic subrang and the shonkinite in the sodipotassic subrang of the wyomingase rang.

None of the minettes of which reliable chemical analyses are available falls near washingtonose in the quantitative classification. The three rocks of this type included in Washington's tables contain from 50·81 to 52·26 per cent of silica. Consequently they are all in the dosalane class. Owing to their relative richness in silica and alumina as compared with the rock here described, their norms are more feldspathic and all are in the perfelic or Germanare order. These norms, from the tables, are as follows:

Norms of Minettes.

	I	II	III
Or	22·8	25·6	41·4
Ab	23·6	32·0	8·4
An	14·2	9·5	16·1
Ne	---	8·8	---
Di	14·8	5·3	3·9
Hy	7·0	---	5·4
Ol	8·0	5·6	14·7
Mt	3·9	5·1	3·5
Il	1·1	3·2	3·2
Ap	1·1	2·5	1·4

I. Augite-minette (Pirsson). Monzonose. W. T. Prof. Paper 14, p. 255.
II. Soda-minette (Brögger). Akerose. W. T., p. 263.
III. Augite-minette (Doss). Dopotassic subrang of andase. W. T., p. 265.

All of these norms contain considerable albite, the quantity reaching 23·6 per cent in the augite-minette (monzonose) from the Little Belt Mountains, Montana, described by Pirsson (I), whereas in the washingtonose here described there is no normative albite. The three norms just given also contain much more anorthite than that of the rock from the banks of the Columbia, but show no normative leucite. Other differences will appear in comparing these norms with that of washingtonose.

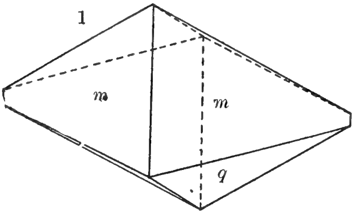
The actual mineralogical composition, or mode, of the washingtonose described can not be accurately calculated, as the compositions of the augite and biotite are not known. The abundance of lenads in the norm, conditioned by the low silica and high alkalies, suggests modal nephelite. None, however, has been detected, while it is certain, on the other hand, that the albite molecule is present in the feldspar. It is, therefore, to be concluded that the actual development of the abundant biotite in the rock leaves available sufficient silica to form albite rather than nephelite. A rough calculation of the mode, in which the pyroxene is figured as ideal diopside and the biotite as one having the ratios

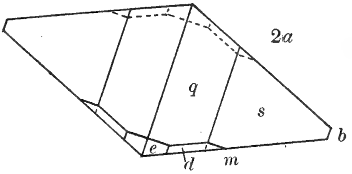
$$\frac{MgO}{K_2O}=4, \quad \frac{FeO}{K_2O}=1, \quad \text{and} \quad \frac{SiO_2}{K_2O}=6,$$

although not accurate enough to give the mode of the rock, shows that, when biotite is allowed for, the readjustment of the constituents locks up sufficient potash and disengages enough silica to raise the remaining lenads to feldspar.

ART. XXXIX.—*Kröhnkite, Natrochalcite (a new mineral), and other Sulphates from Chile;* by CHARLES PALACHE and C. H. WARREN.

THE minerals briefly described in this paper* were sent to the Harvard Mineralogical Laboratory for identification by the Foote Mineral Co. of Philadelphia, whose manager, when the scientific interest of the material was pointed out, at once placed at our disposition all of the material in his possession with generous permission to use whatever was necessary for the investigation.

1




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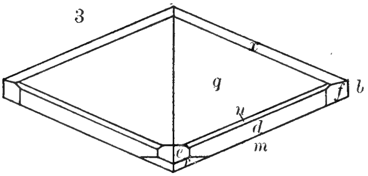

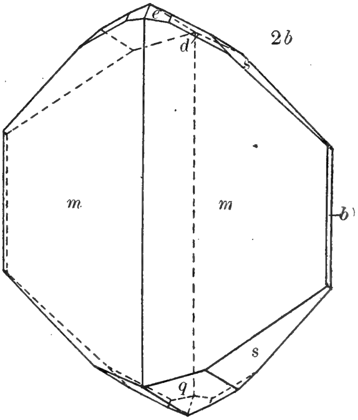

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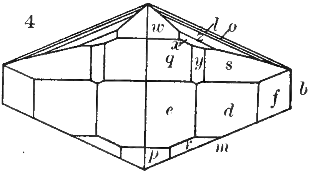

The collection comes from the mining district of Chuquicamata in the Province of Antofagasta, Chile. It was obtained from exhausted copper veins and includes the following species: kröhnkite, natrochalcite (a new mineral), blödite, brochantite, atacamite, chalcanthite, copiatite, botryogen, sideronatrite, halite and gypsum.

Kröhnkite.

Kröhnkite is the most abundant mineral in the collection and appears in three distinct habits, as follows:

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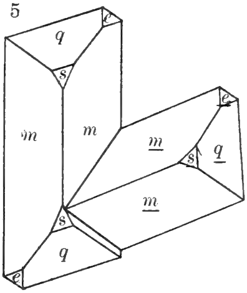
* A more extended crystallographic description of this material will appear hortly in Zeitschrift für Krystallographie.

Phase a.—Clusters of octahedroid crystals of the type of figure 1 but mostly in twin groups, the crystals firmly aggregated to a highly cellular mass, largely infilled with an earthy yellow iron sulphate which may be copiapite. These crystals reach a diameter of $1{\cdot}5^{cm}$ and are of a dull greenish blue color with smooth but lusterless faces.

Phase b.—Single crystals and fibrous or acicular aggregates of pale blue color, implanted on the white quartzose vein material. The crystals are slender prisms with the forms of figure 1 but with the prism largely developed and its planes much curved and facetted through the presence of steep vicinal pyramids. Single crystals reach a length of 4^{cm}.

5



Phase c.—Solid crusts up to 2^{cm} in thickness of deep vitriol blue color, the crystals composing the mass often large and either short or long prismatic, with the forms of figure 2. In cavities on the surfaces of such crusts is a second generation of prismatic crystals of pale blue color, beautifully crystallized and showing the complex combinations of figures 3 and 4. Twin crystals of the type shown in figure 5 are also found on this deep blue material.

The position adopted for the crystals differs from that given by Dana, front and back being interchanged. The axial ratio calculated from measurements on a number of crystals is

$$\breve{a} : \bar{b} : \breve{c} = 0{\cdot}5229 : 1 : 0{\cdot}4357 \quad \beta = 56^\circ\ 17'\ 20''$$

The observed forms are as follows:—*a*(100), *b*(010), *m*(110), *h*(120), *k*(130), *e*(011), *d*(021), *f*(031), $t\,(\bar{1}01)$, $u(\bar{3}02)$, $v(\bar{3}01)$, *p*(111), *r*(121), $q(\bar{1}11)$, $s(\bar{1}21)$, $w(\bar{2}11)$, $x(\bar{2}21)$, $z(\bar{3}31)$, $i(\bar{5}51)$, $o(\bar{1}\bar{0}{\cdot}10{\cdot}1)$, $y(\bar{2}32)$, $n(\bar{1}32)$.

(Tables of measured and calculated angles and combinations will be found in the paper cited above.)

Twinning.—The twin plane is the base, (001). Twins are either contact or interpenetrating, the latter resembling parallel growths owing to peculiarities of angles and distortion.

Cleavage.—Cleavage is perfect and easy parallel to $b(010)$ and good but not so easily produced parallel to $c(011)$. No trace of a prism cleavage as recorded by Darapsky could be detected. Hardness is a little less than 3, just scratched by the finger nail. Specific gravity is 2·061 (Warren), determined in absolute alcohol and calculated for water at 4°C.

Optical Characters, determined by H. E. Merwin.—The principal indices of refraction, determined by means of the refractometer, are : $\alpha = 1{\cdot}5437$, $\beta = 1{\cdot}5775$, $\gamma = 1{\cdot}6013$ for sodium light. $2V_{na}$ calculated from the refractive indices is 78° 36′; from observation of the acute optic angle in oil 78°42′.

The plane of the optic axes is in the plane of symmetry, with the acute bisectrix for yellow (ether-axis a) inclined 48° 45′ to the crystallographic axis $\dot{c}$ in the obtuse angle β. The dispersion, as determined by the colored hyperbolas of interference figures, is inclined. The acute bisectrix for blue is nearer c than the bisectrix for red. The optic axes also are slightly dispersed, more for blue than for red, as indicated by broader color fringes on the hyperbola emerging nearly perpendicular to $\dot{c}$.

Chemical Composition, with analysis by C. H. Warren.—Analysis of the very pure material available confirms the composition of the mineral as given by earlier writers.

$$CuSO_4.Na_2SO_4 + 2H_2O.$$

Most of the water is given off below 150°. Small additional amounts continue to come off up to 350°, when dehydration is complete. The residue may be brought to complete fusion without further decomposition, yielding a bright green enamel.

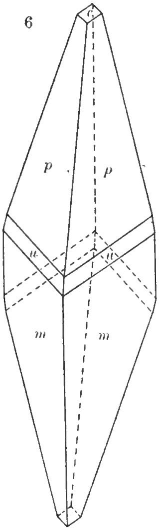
	Per cent.	Mol. Ratio.		Theory.
CuO	23·25	·292	·98	23·49
Na_2O	18·89	·304	1·02	18·39
SO_3	47·60	·595	2·00	47·44
H_2O	10·72	·595	2·00	10·68
Atacamite	trace			
	100·46			100·00

Paragenesis.—Kröhnkite is the most abundant sulphate in these specimens and the first to be formed. Atacamite alone of the few associated minerals may be older, thin crusts of it sometimes lying between the kröhnkite and the vein matrix. Crystals of kröhnkite also show occasional inclusions of copiapite, brochantite and atacamite; none of the other minerals mentioned above as occurring in the collection is found with kröhnkite.

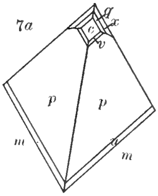
Natrochalcite, a new mineral.

Bright emerald-green crystals of what proves to be a new hydrous double sulphate of copper and sodium were found on several specimens. The crystals are either isolated or in closely adhering crusts upon the white vein matrix; in one specimen they are embedded in chalcanthite and doubly terminated crystals were obtained by carefully breaking away the enclosing blue vitriol. The mineral is monoclinic with a striking pyramidal habit, shown in figure 6; the crystals attain a length of about 1^{cm} and are generally attached to the matrix in such a way that portions of both prism and pyramid are developed; an oscillatory striation parallel to intersection edge of these forms, due to the development of steeper pyramids between them, is generally well marked. A small basal pinacoid and the other faces shown in figure 7, but of minute size, are generally present. The faces proved to be of good quality in most cases and the measurement of six crystals, mostly very small and one of them doubly terminated, yielded satisfactory data for calculation of the elements. For this purpose 45 faces of seven forms were available.

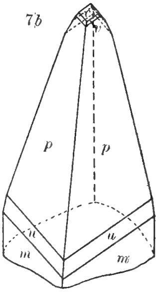
6



7a



7b



$$p_0 = \cdot 8526 \qquad q_0 = 1{\cdot}065 \qquad \mu = 61° \, 17' \, 30''$$

from which was calculated

$$\grave{a} : \bar{b} : \dot{c} = 1{\cdot}423 : 1 : 1{\cdot}214 \quad \beta = 61° \, 17' \, 30''$$

The table contains the forms found, the angles calculated from the elements and the observed angles with their range of variation. It will be seen that the calculated and observed angles show a very satisfactory agreement.

Natrochalcite.—Table of Angles.

		Calculated.		Measured.		Limits.		No. of faces
		ϕ	ρ	ϕ	ρ	ϕ	ρ	
c	001	90°00′	28°42′	90°00′	28°41′	------------	28°39′ 23°42′	3
b	010	00 00	90 00	00 00	90 00	------------	------------	4
m	110	38 41	90 00	38 41	90 00	38°40′–38°43′	------------	12
p	111	51 23	62 47	51 23	62 47	51 15–51 31	62°45–62 50	11
v	112	59 35	50 10	59 35	50 09	59 28–59 44	50 07–50 12	3
u	221	45 45	73 58	45 55	73 39	45 41–46 01	73 14–74 11	5
w	331	43 34	78 45	43 35	78 55	------------	------------	1
q	$\bar{1}11$	$\overline{19}$ 16	52 08	$\overline{19}$ 16	52 08	19 12–19 20	52 06–52 10	7
x	$\bar{2}21$	$\overline{29}$ 54	70 21	$\overline{29}$ 56	70 17	29 50–30 04	70 13–70 21	5

The habit of the crystals is always dominated by the forms chosen as prism and pyramid, *m* and *p*; all other forms are developed with but small faces and often without the full number of their faces.

Cleavage.—Cleavage is perfect and easy parallel to the base, (001). Hardness 4·5, scratching fluorite easily and not scratched by it. Specific gravity 2·33, determined by Warren.

Optical Characters determined by H. E. Merwin.—The principal indices of refraction, determined by means of the reflectometer, and the optic angle for sodium light, are as follows: $\alpha = 1{\cdot}6491$, $\beta = 1{\cdot}6555$, $\gamma = 1{\cdot}7143$. $2V_{na}$, calculated from the refractive indices, 36° 52′; by observation of obtuse optic angle in oil, 36° 48′.

The plane of the optic axes is in the plane of symmetry, the acute bisectrix for yellow being inclined to the crystallographic axis $\dot{c}$ 12° in the acute angle β. The acute bisectrix is the axis *c*; the mineral is therefore optically positive. Dispersion of the optic axes is strong, the acute optic angle for the strongest blue rays transmitted by cobalt glass being 3° greater than the corresponding angle for yellow. There is also a slight inclined dispersion of the acute bisectrix, that for blue lying nearer $\dot{c}$ than that for red.

Chemical Composition.—The composition of the mineral may be expressed by the formula

$$Na_2SO_4.Cu_4(OH)_2(SO_4)_2+2H_2O.$$

The water is given off gradually on continued heating above 150°. The mineral decomposes and gives off SO_3 between 350° and incipient redness. Before the blowpipe it decrepitates and fuses very easily (about 1) to a black bead. Gives off acid water in closed tube, fusing to a dark enamel. It is very slowly dissolved by water and easily by acids.

The analysis which follows was made on less than one gram of material and is not wholly satisfactory to Dr. Warren, the analyst; lack of available substance, however, except at the expense of one of the two remaining specimens, made it seem well to publish it as it stands, subject to revision later should more of the mineral be discovered.

	Per cent.	Mol. Ratio.		Theory.
CuO	41·95	·528	4·00	42·08
Na_2O	8·44	·136	1·03	8·24
SO_3	42·10	·526	4·00	42·51
H_2O	7·70	·427	3·23	7·17
Insoluble res.	·70			
Cl from atacamite	·05			
	100·94			100·00

Paragenesis.—Natrochalcite does not occur with kröhnkite in these specimens, but takes its place, bearing the same age relations to atacamite and brochantite which occur sparingly with it. As above mentioned, it is embedded in chalcanthite in one specimen.

Blödite.—Blödite was identified by the following analysis. It is a massive granular form of the mineral, white where not stained blue by chalcanthite or pale green by finely divided atacamite. It showed no trace of crystalline form. In one specimen it was accompanied by halite and kröhnkite.

Composition, analysis by C. H. Warren:

	Per cent.	Mol. Ratio.		Theory.
MgO	12·00	·300	1·00	11·48
Na_2O	18·20	·296	0·98	18·56
SO_3	47·49	·593	1·98	47·90
H_2O	21·60	1·20	4·00	21·56
Insol.-atacamite and quartz,	·50			
	99·70			100·00

leading to the usual formula, $MgSO_4.Na_2SO_4+4H_2O$.

Of the remaining minerals listed on the first page as occurring in this material there is little to note of special interest. Brochantite is sparingly present in acicular crystals implanted on or surrounded by kröhnkite. Atacamite is in green and deep blue-black crystals of ordinary prismatic and tabular habits; also in crystals elongated parallel to the brachyaxis with nearly equal development of the forms *m*, *e*, *r* and *n*. Chalcanthite is in the form of granular crusts, copiapite and botryogen in granular masses of no distinct form and sideronatrite in yellow needles. Halite in small cubes was present on one specimen of blödite and gypsum is shown in a coarse granular form saturated with finely divided hematite and also in aborescent crystallizations of snow-white color, closely resembling cave-formations of calcite.

Cambridge, June, 1908.

ART. XL.—*On the Measurement of Extinction Angles in the Thin Section;* by FRED. EUGENE WRIGHT.

1. The Measurement of Extinction Angles of Minerals in the Thin Section.
2. The Adjustment of the Petrographic Microscope with Special Reference to the Measurement of Extinction Angles.
3. A Device for Holding Minute Crystals.

1. The Measurement of Extinction Angles of Minerals in the Thin Section.

THE petrographic microscope as an instrument has undergone many changes and modifications since its introduction nearly forty years ago, but from the very first, each improvement has tended to increase its efficiency in such a way that the optical features of minerals in the thin section can be ascertained more readily and more accurately. In the hands of geologists, the microscope is merely the means to an end—an apparatus to aid in recognizing the minerals composing a given rock (mineral composition) and the relations of such rock components to each other (rock texture); and for such purposes the modern petrographic microscope is admirably adapted, especially since, as a rule, approximate results only are required. But with the increased knowledge of rocks thus attained, the demand for data which are precise and quantitative in character rather than qualitative has become more imperative, with the result that, at the present time, one expects to find in a thorough petrographic investigation accurately determined optical constants of each of the rock-forming minerals examined, and in critical points, the probable error of each determination given. This passage from qualitative to quantitative work implies consequences of profound importance; an additional burden is placed on the working geologist, and the time and energy required for the investigation of a given problem is much greater under the present régime than formerly; at the same time, this transition indicates that, in one phase of geology, at least, the step from the lower first plane of preliminary reconnaissance work to the higher level of precise and detailed work is being taken.

The optical properties which are made use of in the practical determination of minerals under the microscope are, briefly: refractive index, birefringence, optical axial angle, optical character, extinction angles, color and pleochroism. By means of these properties alone it is possible to ascertain the crystal system to which a given mineral belongs, and by a short process of elimination to determine definitely the mineral in question. This process has been carried to such refinement in certain instances, as in the isomorphous series of plagioclase feldspars, that it is now possible, from extinction angles alone, to determine very closely the actual chemical composition of the particular plagioclase in hand.

For a given mineral plate in the thin section, the term extinction angle signifies the angle between a known crystallographic direction (cleavage line, or trace of a crystal face on that plate) and one of its optic ellipsoidal axes or directions along which it extinguishes when these directions are parallel with the principal planes of the crossed nicols. In order to ascertain this angle satisfactorily one must be able not only to measure plane angles accurately, but also to locate correctly the position of the optic ellipsoidal axes of the particular crystal plate. The first condition is easily accomplished and demands no special comment, while the second requirement is extremely difficult to meet with any degree of satisfaction without great expenditure of time.

Many methods have been suggested by which the position of the optic ellipsoidal axes of a given crystal section can be located more or less exactly, and all are based on the fact that when the optic ellipsoidal axes are parallel with the principal planes of the crossed nicols the plane polarized light normally incident from the lower nicol passes through the crystal plate without changing its plane of vibration. In case the optic ellipsoidal axes of the plate do not coincide with the planes of the nicols, interference in general takes place and some light passes through the upper nicol. The different methods proposed have for their common object the rendering apparent the extremely small percentage of light which thus emerges from the analyzer when the angle of revolution of the crystal plate from its position of absolute darkness is very small.

Before considering in detail the different methods for accomplishing this result and their relative merits and defects, it will be well to treat the subject mathematically and to derive the formulas for the intensity of light with special reference to the subject of extinction angles. This treatment is given in some detail in the following paragraphs, since the deductions given later are all drawn from these fundamental equations.

Theoretical.

Mathematical.—The phenomena of light are considered to be produced by periodic changes or disturbances in the ether, transverse to the direction of propagation. Different hypotheses have been proposed which assign different properties to this medium, but no one of the hypotheses yet suggested is satisfactory in all its details.* For the purposes of this paper, however, these disturbances may be considered vibrations of ether particles about positions of rest and in a plane normal to the line of wave propagation. Adopting this view chiefly as a matter of easy expression, we may assert that in plane polarized light the disturbances or vibrations are confined to a plane, each particle vibrating then with simple periodic motion, to and fro, pendulum like, along a straight line. An equation which satisfies such a periodic vibration and which has been found to represent satisfactorily the ether disturbances, is the following:

$$y = a \sin \frac{2\pi}{T} (t - t_1) \tag{1}$$

in which a represents the amplitude, T the periodic time, $\frac{2\pi t_1}{T}$ the initial phase, t the time which has elapsed at any given instant, and y the distance of the ether particle from its position of rest. The velocity of the ether particle at any instant is given by

$$v = \frac{dy}{dt} = a \frac{2\pi}{T} \cos \frac{2\pi}{T} (t - t_1)$$

and if m be its mass, its kinetic energy is $1/2\ mv^2$.

The above equation shows that v varies from 0 to $\frac{2\pi a}{T}$; accordingly the average kinetic energy during a complete vibration will be

$$\frac{1}{T}\int_0^T 1/2\ mv^2 dt = \frac{ma^2\pi^2}{T^3}\int_0^T 2\cos^2 \frac{2\pi}{T}(t - t_1)\, dt$$

$$= \frac{ma^2\pi^2}{T^3}\int_0^T \left(1 + \cos \frac{4\pi}{T}(t - t_1)\right) dt = \frac{ma^2\pi^2}{T^3}\left[t + \frac{t}{4\pi}\sin\frac{4\pi}{T}(t - t_1)\right]_0^T$$

$$= \frac{ma^2\pi^2}{T^2}.$$

Now, a vibrating particle possesses at any instant a definite amount of kinetic energy and also a definite amount of potential energy, and the sum of these two amounts of energy remains constant throughout the vibration, so that as the kinetic energy in the particle increases its potential energy

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* These theories, as well as the mathematical treatment of the same, are given in the standard text-books on light (Preston's Theory of Light; P. Drude, Lehrbuch d. Optik, and many others; also Rosenbusch-Wülfing, Mikrosk. Physiographie i, 1; and Duparc and Pearce, Traité de Technique Minéralogique et Pétrographique).

decreases, and vice versa. At the moment the kinetic energy of the particle becomes zero, the total energy is potential, and similarly, when the kinetic energy attains its maximum, the potential energy is zero. In other words, the average potential energy is equal to the average kinetic energy, and the whole energy is twice the average kinetic energy, given in the above expression.

A measure for the intensity of light is the energy per unit volume of the vibrating ether, and if in the above expression for the kinetic energy m stands for the mass per unit volume, the whole energy or intensity will be measured by the expression,

$$\mathrm{I} = \frac{2m\pi^2a^2}{\mathrm{T}^2}$$

In practice, only relative intensities are encountered. The relative intensities of two light vibrations of equal period (T) at a given point will be in the ratio of the square of their amplitudes:

$$\frac{\mathrm{I}_1}{\mathrm{I}_2} = \frac{2m\pi^2a_1^{\,2}}{\mathrm{T}^2} \div \frac{2m\pi^2a_2^{\,2}}{\mathrm{T}^2} = \frac{a_1^{\,2}}{a_2^{\,2}} \qquad (2)$$

In other words, the intensity of light of a given period of vibration (color) varies as the square of its amplitude (a) of vibration.

This relation will now be made use in determining the relative intensities of the plane polarized light waves which emerge from the upper nicol of the microscope, after having passed through the lower nicol and an intervening crystal plate in different positions.

Disturbances in the ether which produce light phenomena are ascribed to the action of forces on the ether mass, and if two or more separate disturbances are simultaneously impressed on the same element, the resultant disturbance can be calculated according to the principle of the resolution of forces on the assumption of direct superposition of the forces. If, in the case of plane polarized light, two separate vibrations be imposed simultaneously on an element, the resultant vibration will also be in that plane, and its amplitude, on the principle of superposition, is the algebraic sum of the amplitudes of the components. The mathematical expression for the resultant vibration of a particle simultaneously impressed by two periodic disturbances of the same period but differing in phase and amplitude, can be deduced from the equations of the separate vibrations.

$$y_1 = a_1 \frac{\sin 2\pi\,(t-t_1)}{\mathrm{T}} \text{ and } y_2 = a_2 \sin \frac{2\pi\,(t-t_2)}{\mathrm{T}}$$

The resultant displacement at any time t is

$$y=y_1+y_2=a_1 \sin\frac{2\pi}{T}(t-t_1)+a_2 \sin\frac{2\pi}{T}(t-t_2)$$

$$=\sin\frac{2\pi}{T}t(a_1 \cos\frac{2\pi}{T}t_1+a_2 \cos\frac{2\pi}{T}t_2)-\cos\frac{2\pi}{T}t(a_1 \sin\frac{2\pi}{T}t_1+a_2 \sin\frac{2\pi}{T}t_2)$$

$$=A \sin\frac{2\pi}{T}(t-t_3)$$

if

$$A \cos t_3=a_1 \cos\frac{2\pi}{T}t_1+a_2 \cos 2\pi t_2$$

and

$$A \sin t_3=a_1 \sin\frac{2\pi}{T}t_1+a_2 \sin\frac{2\pi}{T}t_2$$

By squaring and adding the last two expressions, we obtain

$$A^2=a_1^2+a_2^2+2a_1a_2 \cos\frac{2\pi}{T}(t_2-t_1) \qquad (3)$$

In this expression $\frac{2\pi}{T}(t_2-t_1)$ denotes the difference in phase of the two component periodic displacements and A the amplitude of the resultant vibration.

In considering the effects which different crystals exert on transmitted light waves, it has been found, both in practice and theory, that these influences can be predicted accurately and satisfactorily by reference to a triaxial ellipsoid, the optical ellipsoid, the position and relative axial lengths of which vary in general with different minerals, and with the wave length of light employed. Thus the directions of vibration of light waves emerging normally from a mineral plate are parallel with the major and minor axes of the ellipse which a central diametral plane parallel to the given plate cuts out of the optical ellipsoid for the particular mineral and wave length used. The determination of the actual position of these directions in the plate is accomplished in polarized light by observing the relative intensity of the transmitted light for different positions of the plate parallel to the principal planes of the nicols.

Light waves emerging from the lower nicol are plane polarized and their vibration is given by the equation

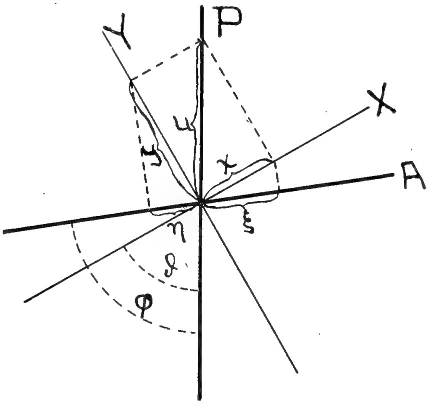
$$u=a \sin\frac{2\pi t}{T}$$

On entering the crystal plate, this vibration is resolved into two vibrations in planes normal to each other. If θ (fig. 1) be the angle included between the major optic ellipsoidal exis of the plate and the plane of the incident vibrations, the equations for the resultant waves are

$$x = u \cos\theta = a \cos\theta \sin\frac{2\pi t}{T} \text{ and } y = u \sin\theta = a \sin\theta \sin\frac{2\pi t}{T}$$

Each of these vibrations traverses the plate with a different velocity and the time required by the fast wave to traverse the plate of thickness d will be $t_1 = d.a^1$, while the time required by the slow wave is $t_2 = d.\gamma^1$ where a^1 and γ^1 are respectively the refractive indices of the two waves. On emergence, therefore, the equations for the periodic displacements will be

FIG. 1.



$$x^1 = a \cos\theta \sin\frac{2\pi}{T}(t - da^1) \text{ and } y^1 = a \sin\theta \sin\frac{2\pi}{T}(t - d\gamma^1)$$

On reaching the upper nicol each of these vibrations is again resolved further into two component vibrations again normal to each other, one of which, however, is annulled by total reflection. If ϕ be the angle between the principal planes of the nicols, then the component vibrations emerging from the upper nicol are

$$\xi = x^1 \cos(\theta - \phi) = a \cos(\theta - \phi) \cos\theta \sin\frac{2\pi}{T}(t - da^1) = A_1 \sin\frac{2\pi}{T}(t - da^1)$$

$$\eta = y^1 \sin(\theta - \phi) = a \sin(\theta - \phi) \sin\theta \sin\frac{2\pi}{T}(t - d\gamma^1) = A_2 \sin\frac{2\pi}{T}(t - d\gamma^1)$$

and the resultant amplitude

$$A = \xi + \eta = A_1 \sin\frac{2\pi}{T}(t - da^1) + A_2 \sin\frac{2\pi}{T}(t - d\gamma^1)$$

The intensity I^1 of the emergent wave is then proportional to the square of the amplitude

$$\frac{I^1}{I} = \frac{A^2}{a^2}$$

The equations (3) above, moreover, show that

$$A^2 = A_1{}^2 + A_2{}^2 + 2\,A_1 A_2 \cos\frac{2\pi}{T}\,d\,(\gamma^1 - \alpha^1)$$

On substituting the values of A_1 and A_2 in this equation, and noting that

$$\cos\frac{2\pi}{T}\,d(\gamma^1 - \alpha^1) = 1 - 2\sin^2\frac{\pi}{T}\,d\,(\gamma^1 - \alpha^1)$$

we obtain $A^2 = a^2\,[\cos^2\phi - \sin 2(\theta - \phi)\sin 2\theta \sin^2\frac{\pi}{T}\,d\,(\gamma^1 - \alpha^1)]$ (4)

and finally, $\frac{I^1}{I} = \frac{A^2}{a^2} = \cos^2\phi - \sin 2(\theta - \phi)\sin 2\theta \sin^2\pi d\,(\gamma^1 - \alpha^1)$ (5)

But the velocity of light V, period of vibration T, and wave length λ, are so related that VT = λ and if we consider the velocity unity, then we may replace T by λ and the equation (5) reads:

$$\frac{I^1}{I} = I_1 = \cos^2\phi - \sin 2\,(\theta - \phi)\sin 2\theta \sin^2\frac{\pi}{\lambda}\,d\,(\gamma^1 - \alpha^1)$$

This is the usual expression for the relative intensity of the emergent waves; it may, however, be brought into more convenient form for practical purposes. To save space, let $\sin^2\frac{\pi d}{\lambda}(\gamma^1 - \alpha^1) = K$, where K may have any value from 0 to + 1; then

$$I_1 = \frac{1 + \cos 2\phi}{2} - K \sin 2\theta \sin 2(\theta - \phi)$$

$$\begin{aligned} 2I_1 &= 1 + \cos 2\phi - 2K \sin 2\theta \sin 2(\theta - \phi) && \text{(a)} \\ &= 1 + \cos 2\phi - K\,(\cos 2\phi\,(1 - \cos 4\theta) - \sin 2\phi \sin 4\theta) && \text{(b)} \\ &= 1 + (1 - K)\cos 2\phi + K \cos 2(\phi - 2\theta) && \text{(6)} \end{aligned}$$

For a given angle θ to find the condition that the intensity will be zero, the equation (*a*) of the foregoing can be changed to

$$\begin{aligned} 2I_1 &= 1 + (1 - 2K\sin^2 2\theta)\cos 2\phi + 2K \sin 2\theta \cos 2\theta \sin 2\phi \\ &= 1 + K_1 \cos 2\phi + K_2 \sin 2\phi && \text{(7)} \end{aligned}$$

in which

$$K_1 = 1 - 2K\sin^2 2\theta \text{ and } K_2 = 2K \sin 2\theta \cos 2\theta.$$

If $2I_1 = 0$, then

$$1+K_1 \cos 2\phi+K_2 \sin 2\phi=0$$

$$\text{or } 1+K_1 \cos 2\phi=-K_2 \sin 2\phi$$

squaring $1+2K_1 \cos 2\phi+K_1^2 \cos^2 2\phi= K_2^2 - K_2^2 \cos^2 2\phi$

$$\cos 2\phi=\frac{-K_1}{K_1^2+K_2^2} \pm \sqrt{\left(\frac{K_1}{K_1^2+K_2^2}\right)^2+\frac{K_2^2-1}{K_1^2+K_2^2}} =$$

$$\frac{-K_1}{K_1^2+K_2^2} \pm \frac{K_2^2}{K_1^2+K_2^2}\sqrt{K_1^2+K_2^2-1} \qquad (8)$$

In order that $\cos 2\phi$ have a real value, the expression $K_1^2+K^2-1$ must be zero or positive. But,

$$K_1^2=1-4\,K \sin^2 2\theta+4K^2 \sin^4 2\theta$$
$$K_2^2=\quad 4\,K^2 \sin^2 2\theta-4K^2 \sin^4 2\theta.$$

Accordingly,

$$K_1^2+K_2^2-1 = \quad -4K \sin^2 2\theta\,(1-K) \qquad (9).$$

The right hand of this equation is a negative quantity, and $\cos 2\phi$ can have a real value only when $K_1^2+K_2^2-1=0$, and this condition is fulfilled only when

(1) $K=0$; *or* $\sin^2 \frac{2\pi}{T} d\,(\gamma^1-\alpha^1) = 0$, i. e. $\frac{\pi}{T} d\,(\gamma^1-\alpha^1) =n\pi$

(2) $K=1$; *or* $\sin^2 \frac{2\pi}{T} d\,(\gamma^1-\alpha^1)=1$, i. e. $\frac{\pi}{T} d\,(\gamma^1-\alpha^1)=(n+1)\frac{\pi}{2}$

(3) $\sin^2 2\theta=0$; i. e. $\theta=n\,\pi$.

The value for $\cos 2\phi$ then reduces to

$$\cos 2\phi=\frac{-K_1}{K_1^2+K_2^2}=-K_1=-(1-2K \sin^2 2\theta)$$

For the three different cases the value of $\cos 2\phi$ becomes

(1) $\cos 2\phi = -1$ i. e. $\phi = (2n+1)\frac{\pi}{2}$

(2) $\cos 2\phi = -(1-2 \sin^2 2\theta) = -\cos 4\theta$, i. e. $\phi=\pi-2\theta$

(3) $\cos 2\phi = -1$ i. e., $\phi = (2n + 1)\frac{\pi}{2}$

If the nicols be not crossed, therefore, it is not possible to obtain absolute darkness for a given section unless $2\frac{\pi d\,(\gamma^1-\alpha^1)}{T} = \frac{(2n+1)\,\pi}{2}$ i. e., unless monochromatic light be used of such a wave length that the one wave is an odd number of half wave lengths ahead of the second, and in this case, $\phi=\pi-2\theta$. If white light be employed, abnormal interference colors will appear because of the abnormal conditions, and at no point will darkness ensue.

The condition that the entire light be transmitted is

$$I_1 = \frac{I^1}{I} = 1$$

or $$(1-K)\cos 2\phi + K\cos 2(\phi - 2\theta) = 1$$
which is satisfied if both $\phi = 0$ and $\theta = 0$.

In case either ϕ or θ be given, the problem of finding the particular disposition of upper nicol or crystal plate for which the intensity of the transmitted light reduces to a minimum or maximum, involves the first partial differential quotients of the function $2I_1$ (equation 6) after either ϕ or θ. If ϕ be given, the point in question is determined by

$$\frac{\delta(2I_1)}{\delta\ \theta} = 4K \sin 2(\phi - 2\theta) = 0$$
$$\therefore\ \phi = 2\theta \text{ or } \phi = \pi - 2\theta$$

The second partial differential quotient shows that for the first value of θ the intensity is a minimum, while for $\phi = \pi - 2\theta$ the intensity is a maximum. This relation is of importance in certain of the methods described below.

If θ be given and ϕ is the variable,

$$\frac{\delta(2I_1)}{\delta\phi} = \ -2\ (1-K)\sin 2\phi - 2\ K \sin 2\ (\phi - 2\theta) = 0$$

From this equation we find

$$\sin^2 2\phi = \frac{K^2 \sin^2 4\theta}{(1-K)^2 + 2K\ (1-K)\cos 4\theta\ +\ K^2}$$

a complicated expression which for K=1 simplifies to

$$\sin^2 2\phi = \sin^2 4\theta$$ and this equation

is satisfied for
$$\phi = 2\theta$$
$$\phi = \pi - 2\theta$$

It is of interest to plat the values given by the equation for different values of ϕ and θ.

$$2I_1 = 1 + (1-K)\cos 2\phi\ +\ K\cos 2\ (\phi - 2\theta). \qquad (6)$$

In fig. 2, curve V, the rate of increase in intensity of light is given for the special case of $\theta = 0$, where simply the upper nicol is turned and the crystal plate has no effect in the polarization of the waves from the lower nicol. In this case

$$2I_1 = 1 + \cos 2\phi \qquad (10)$$

From the curve it is evident that the rate of increase is very slow at first, but rises rapidly and reaches a flexion point at 45°, after which the intensity increases with decreasing rapidity to its maximum value at 90°.

FIG. 2.

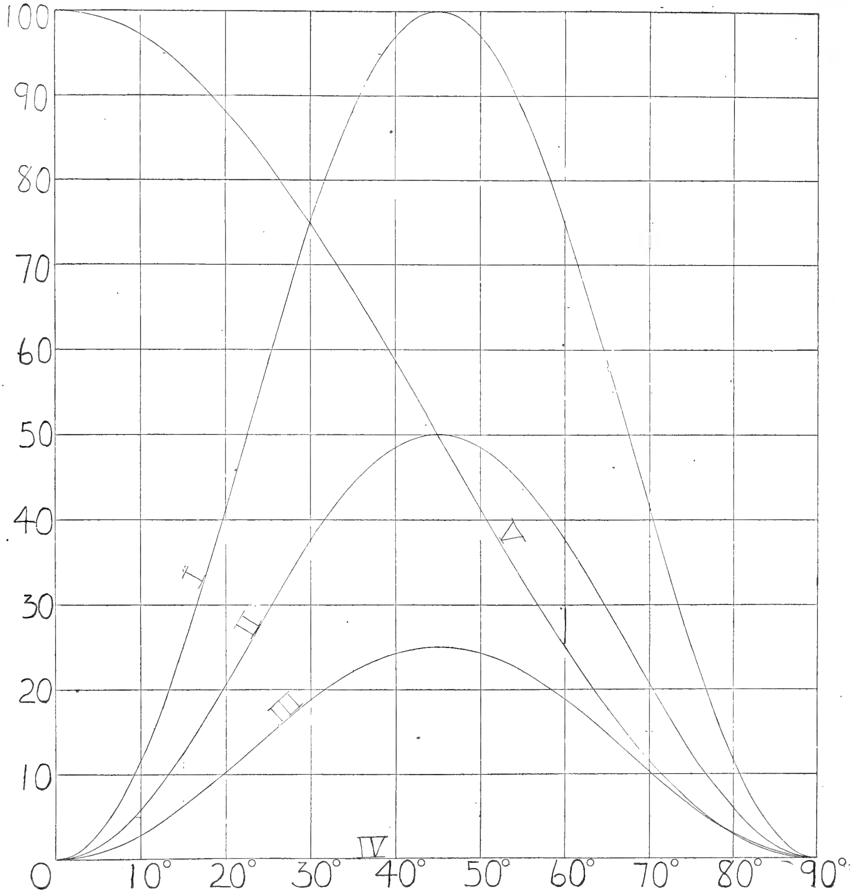


FIG. 2.—Curves showing relative intensity of light emerging from upper nicol after transmission through polarizer, crystal plate and analyzer, the positions of the crystal plate and also the analyzer ranging from 0°–90°. The abscissa values refer to angular distances of the major ellipsoidal axis of the crystal plate and also of the plane of the analyzer. For curves I–IV, the nicols are considered crossed ($\phi = \frac{\pi}{2}$) and the crystal plate alone to be revolved from 0° to 90°. In curve 1, $\sin^2 \frac{2\pi}{T} d\,(\gamma^1 - \alpha^1) = K = 1$; in curve II, $K = 1/2$; in curve III. $K = 1/4$; in curve IV, $K = 0$. Curve V shows the relative intensity of the emerging light for different positions of the analyzer alone ($\theta = 0$, ϕ ranging from 0° to 90°). Curves calculated from the general formula

$$I_1 = 1/2\,(1 + (1-K)\cos 2\phi + K \cos 2(\phi - 2\theta)).$$

In case the nicols are crossed ($\phi = \frac{\pi}{2}$), the rates of increase for different values of K are given by the reduced equation

$$2I_1 = K\,(1 + \cos 4\theta) = 2K \sin^2 2\theta \qquad (11)$$

which defines a curve similar in aspect to the foregoing except that ϕ is replaced by 2θ and the factor K tends to reduce all values proportionately. The curves I–IV of fig. 2 represent the relative intensities for values of $K = 1$, 1/2, 1/4 and 0 respectively. The greatest possible intensity is thus attained when $K = 1$, i. e., when the waves, after emerging from the crystal plate, are an odd number of half wave lengths apart (in opposite phase); the intensity is zero for all positions of the plate when $K = 0$, i. e., when the distance between the two emergent waves is a whole number of wave lengths.

In figs. 3–6, intensity curves are drawn showing the relative intensity of the emergent light for different positions of the crystal plate (θ usually 0°, 15′, 30′, 45′, and 1°) with the principal plane of the lower nicol, and for different positions of the upper nicol (ϕ ranging from 88° to 92°). The heavy curve in each figure is the relative intensity curve of the crystal alone (nicols crossed, $\phi = 90°$) and θ (ranging from $-2°$ to $+2°$) The narrow range of intensities only is considered, since in general it represents about the order of magnitude of the probable error of a single determination made in the usual manner.

In each of the figures the unit ordinate division represents ·025 per cent of the total intensity and the unit abscissa division 10′ of arc.

In fig. 3, K is considered $= 1$ or $\sin^2 2\frac{\pi}{\lambda} d(\gamma^1 - a^1) = 1$, which obtains when the one wave is any odd number of half wave lengths ahead of the second on emergence from the plate; in figs. 4, 5, 6 and 7, the relative intensity curves are drawn for $K = 3/4$, 1/2, 1/4 and 0 respectively.

It is not a difficult matter to grasp the meaning of these curves, as the following example will show: let it be required to find the percentage of light which emerges from the nicol in the case of a mineral plate of such thickness and birefringence that for yellow light the faster waves after emerging from the plate will be precisely one half wave length ahead of the slow waves ($K = 1$, fig. 3), the direction of extinction of the plate to make an angle of 30′ ($\theta = 30'$) with the principal plane of the lower nicol, and the principal plane of the upper nicol to include an angle of 89° 10′ with the lower nicol ($\phi = 89° 10'$) On the 30′ curve of fig. 3 the ordinate for 89° 10′ is ·104 and the relative intensity is therefore ·104 of 1 per cent of the total intensity.

Fig. 3.

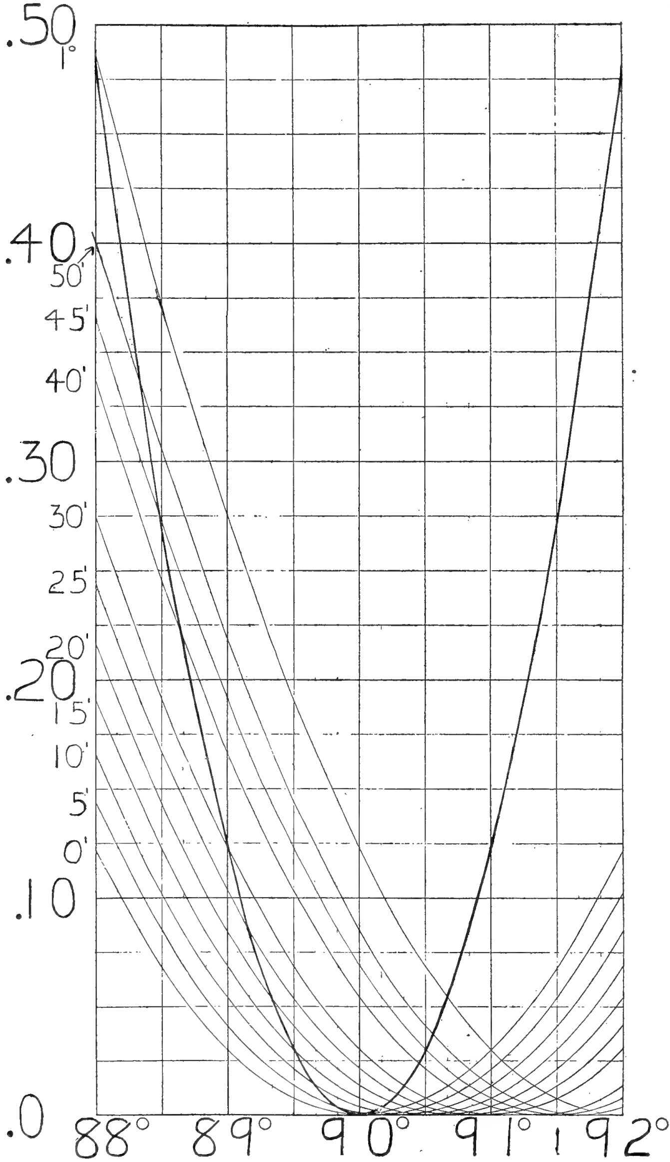


Fig. 3.—Intensity curves for crystal plates making angles 0′, 5′, 10′, 15′, 20′, 25′, 30′, 40′, 45′, 50′ and 1° with plane of polarizer. Analyzer revolved about axis from 88° to 92° with lower nicol plane.

$$\sin^2 \frac{2\pi t}{T} (\gamma'-\alpha')=K=1$$

Curves calculated from the formula

$$I = 1/2 \, (1 + \cos 2 \, (\phi - 2\theta)).$$

The

FIG. 4.

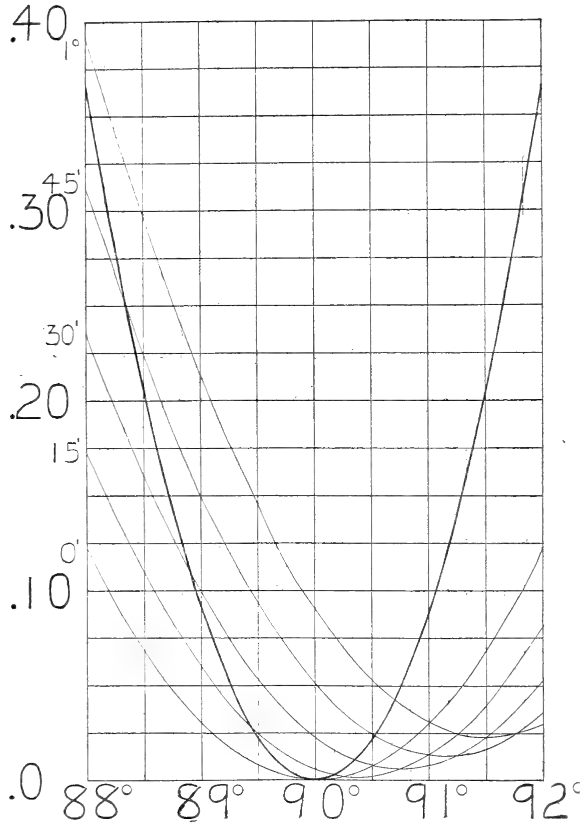


FIG. 4.—Intensity curves for crystal plates at angular distances of 0′, 15′, 30′, 45′, and 1° from plane of polarizer, the analyzer being revolved about axis from 88° to 92° with plane of polarizer. $\sin^2 \frac{2\pi t}{T} (\gamma' - a') = K = 3/4$. Curves calculated from the formula

$$I_1 = 1/8 \left[4 + \cos 2\phi + 3 \cos 2 (\phi - 2\theta) \right].$$

As in fig. 3, the heavy curve indicates the relative intensity of emergent light for different positions of the crystal plate (θ ranging from 88° to 92°, or −2° to +2°) under crossed nicols ($\phi = \frac{\pi}{2}$) and $K = 3/4$. Calculated from the formula

$$I_1 = 3/8 (1 + \cos 4\theta)$$

---

heavy curve indicates the relative light intensity under crossed nicols ($\phi = \frac{\pi}{2}$) for different positions of the crystal plate (θ ranging from 88° to 92° or −2° to +2°) and $K = 1$. Calculated from the formula $2 I_1 = 1 + \cos 4\theta$.

These figures 2–6 are well adapted to show graphically certain facts which are evident from a mathematical consideration of the intensity formula. (1) If $K = 0$, which occurs when the one wave is any number of whole wave lengths ahead of the second, the crystal plate is dark and remains dark for all positions of revolution, as indicated by the heavy abscissa line of fig. 7. (2) In case $K = 1/4$, fig. 6, the intensity curve for crystal plate, coincides very closely with that for the revolving nicol. The extinction curves, moreover, for the crystal plate at different angles ($\theta = 15', 30', 45'$, and $1°$) with the principal plane of the lower nicol and for different positions of the upper nicol (ϕ ranging from 88° to 92°) are similar and lie close together, so that, in this particular case, methods involving the

Fig. 5.

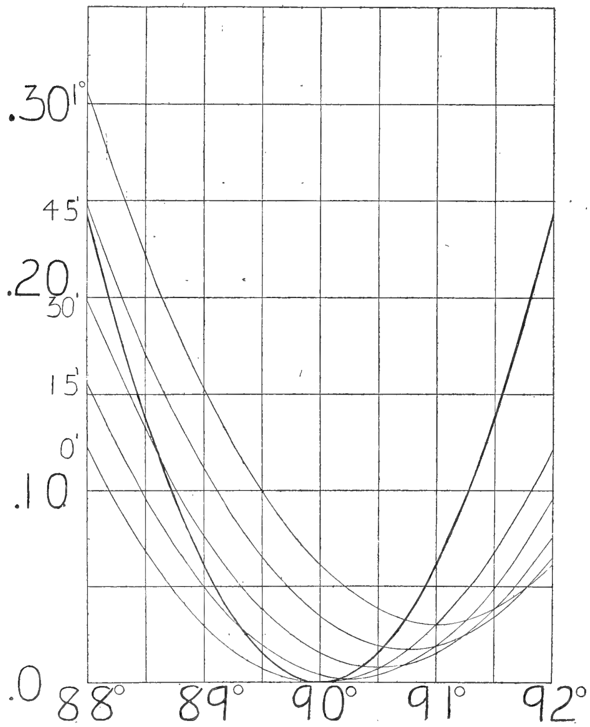


Fig. 5.—This figure differs from the two preceding figures only in the value of K, which is 1/2. The curves were calculated from the formula

$$I_1 = 1/4\ (\ 2 + \cos 2\phi + \cos 2(\phi - 2\theta)\ ).$$

The heavy curve from the formula

$$I_1 = 1/4\ (1 + \cos 4\theta).$$

revolution of the upper nicol for the location of zero intensity directions are not greatly different in their degree of accuracy from those in which the nicols remain crossed and the crystal plate is revolved. Nevertheless, even in this instance the former are the more sensitive methods and results attained by their use are correspondingly more accurate. For K=1/2, fig. 5, the extinction curve for the crystal plate alone (nicols crossed and plate only revolved) no longer coincides with that for the upper nicol alone, but similar conclusions can be drawn as to the relative sensitiveness of the two methods, the one involving the revolution of the crystal plate (while the nicols remain crossed), and the second, the revolution of the upper nicol while the crystal plate remains stationary. The amount of light which is required to produce the sensation of light in the human eye is different for different persons. But for a given eye the limit of the actual sensation of monochromatic light is fixed for any particular instant and may be represented by one of the horizontal percentage lines of the figures. Let us assume that for a source of monochromatic light of definite intensity I, the limit for the sensation of light is ·050 per cent of the

FIG 6.

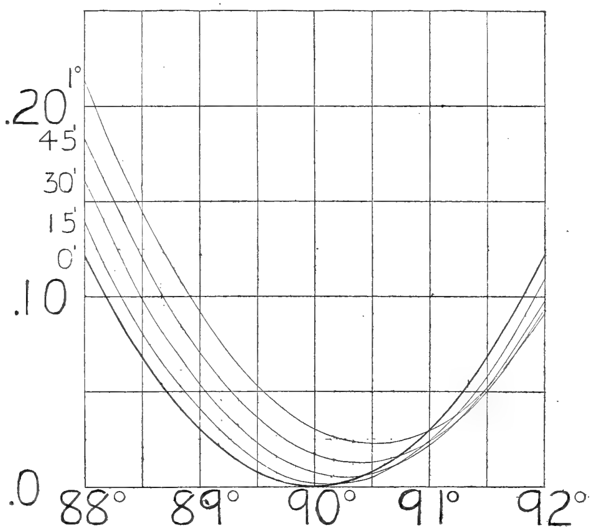


FIG. 6.—Differs from fig. 5 only in K, which is 1/4. The curves are expressed by the formula

$$I_1 = 1/8\,[\,4 + 3\cos 2\phi + \cos 2\,(\phi - 2\theta)\,]$$

and the heavy curve by

$$I_1 = 1/8\,(1 + \cos 4\theta)$$

total intensity and represented by second horizontal line above the base line of fig. 5.

Then the curve for the crystal alone shows that for all points below that line, i. e., between 89° 04′ and 90° 56′, the crystal will appear absolutely dark and on a single determination an error of nearly ±1° may be made. If, however, the crystal plate remain stationary, and the upper nicol be revolved through small angles from its normal, crossed position ($\phi = 88°$ to 92°), it is evident from the figure that if, for example, the crystal plate is 30′ distant from its position of true extinction and still dark under crossed nicols so far as the eye of the observer can detect, the differences in intensity between the field and crystal plate for different angles of revolution of the upper nicol (measured by the ordinate intercepts between the curve 0′ and 30′ of figure), are of such a character that at the point where the illumination of the field can just be observed (88° 43′) the intensity of illumination of the crystal is more than twice as great (·106 per cent instead of ·05 per cent), whereas

FIG. 7.

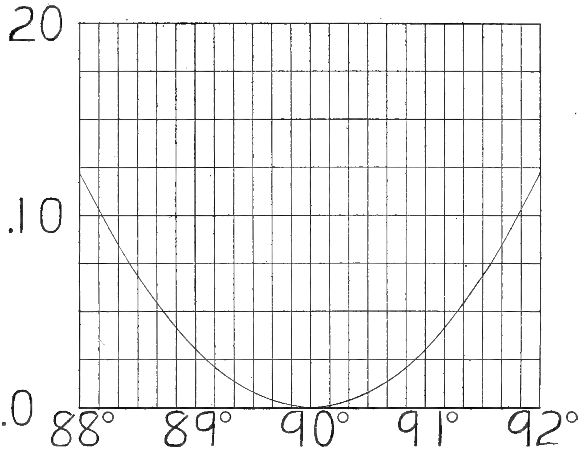


FIG. 7.—In this particular case K is considered = 0 and the general formula reduces to

$$I = \frac{1}{2}(1 + \cos 2\phi)$$

which is independent of θ. In other words, if the thickness of the plate be such that $\sin^2 \frac{2\pi t}{T}(\gamma' - \alpha') = 0$, or the emerging waves are any number of whole wave lengths apart, total interference takes place and the plate is dark under crossed nicols for every angle of revolution about its normal axis.

on the other side, where first indications of illumination on the central plate can be detected at 91° 41′, the field is lighted up by ·085 per cent instead of ·050 per cent of the total intensity. These differences of intensity are of such a character that they can readily be observed, and the sensitiveness of any method involving the revolution of the upper nicol while the crystal remains stationary is in this case at least twice as great as that for which the nicols remain crossed and the crystal plate alone is revolved.

Similar theoretical conclusions can be drawn from figs. 3 and 4.

If white light be used and the upper nicol be revolved abnormal interference colors result. The rapid and pronounced change in interference colors near the position of crossed nicols, on a plate which is not precisely in the position of true extinction, is well adapted for use in the location of its ellipsoidal axes.

With a given color of monochromatic light extinction angles should be determined on plates of such a thickness that K is about +1 (the two emergent waves are a whole number of half wave lengths apart). Thus if sodium light be used the plates should show in white light an interference color of about straw-yellow of the first order but not sensitive violet, since for this particular thickness the two waves are 589$\mu\mu$ apart and the yellow waves are totally destroyed, with the result that the plate appears dark in all positions. It follows, furthermore, that a plate which is well adapted for determinations in one kind of monochromatic light may be useless for another color.

It has been found that the insertion between the crossed nicols of specially cut plates and wedges of birefracting substances, as quartz and selenite, is often well adapted to increase the accuracy of the measurement of the extinction angle on a given plate. The principle there involved is that of the superposition of birefracting plates, the action of which is to produce a resultant which differs from that of either component. It is possible to select a wedge or plate of such a character that the interference phenomena produced by it alone are extremely sensitive to the slight changes produced by a second crystal plate when it is not precisely in the position of true extinction.

From the mathematical standpoint, the insertion of a second plate involves a new set of conditions for the vibrating ether elements and the equations for the resultant are correspondingly more complex. Their derivation, however, is exactly counterpart to that for the intensity of a single crystal plate and the final result only need be given here. If the nicols be crossed and θ_1 be the angle which $\gamma_1{}^1$ of the crystal plate of thickness d_1 includes with the principal plane of the polarizer and θ_2, the angle between γ_2^1 of the inserted plate or wedge of thickness d_2 and the polarizer plane, the relative intensity is given by the formula, and $d_1(\gamma_1^1 - a_1^1) = T_1$ and $d_2(\gamma_2^1 - a_2^1) = T_2$, then

$$
\begin{aligned}
I_1 = {} & \sin 2(\theta_2 - \theta_1) \sin 2\theta_1 \cos 2\theta_2 \sin \frac{2\pi}{T} T_1 \\
& + \sin 2(\theta_2 - \theta_1) \cos 2\theta_2 \sin 2\theta_2 \sin \frac{2\pi}{T} T_2 \\
& + \cos^2 (\theta_2 - \theta_1) \sin 2\theta_1 \sin 2\theta_2 \sin \frac{2\pi}{T} (T_1 - T_2) \\
& - \sin^2 (\theta_2 - \theta_1) \sin 2\theta_1 \sin 2\theta_2 \sin \frac{2\pi}{T} (T_1 - T_2)
\end{aligned}
$$

From this formula the relative intensity can be calculated for any given values of (θ_1, θ_2) and T_1 and T_2.

In case the crystal plate is of such a thickness that $\sin \frac{2\pi}{T} T_1 = 1$ and at the same time the inserted plate is also of a thickness that $\sin \frac{2\pi T_2}{T} = 1$, this equation reduces to

$$I_1 = \sin^2 2(\theta_2 - \theta_1)$$

an expression for a curve similar in every respect to those of fig. 2, but which is zero for $\theta_2 = \theta_1$ and also for $\theta_2 = \frac{\pi}{2} + \theta_1$ and reaches its maximum of 1 at $\theta_2 = \frac{\pi}{2} + \theta_1$. It can also be shown that for a given increment of θ_2 as $d\theta_2$, the ratio of the value of the function for $(\theta_2 + d\theta_2)$ to its value for θ_2 is greatest when θ_2 is equal to θ_1. If, therefore, the angle θ_2 be so chosen that the field is just illuminated, the change resulting from small angles of θ_1 will be greater than for any other position of the inserted plate.

In the Calderon method described below, the calcite plates are purposely so thick that they show the white interference colors of higher orders in white light, in which case the thickness is so great that for a number of different colors throughout the spectrum the path difference of the emergent waves is a whole number of wave lengths, in other words, in the Calderon method it is permissible for practical purposes to consider the plate of such a thickness that for white light the expression $\sin^2 \frac{\pi}{\lambda} T_2$ is unity, and that therefore the angle θ_2 should be small in order to secure the best results, so small in fact that the illumination of the field is just visible.

In several of the other methods cited below for the exact location of the ellipsoidal axes of a given plate, use is made of quartz plates or wedges, cut normally to the principal axis, which rotate the planes of vibration of normally incident, plane polarized light. For the purposes of this paper it is not necessary to enter into the mathematical discussion and theory of the rotatory power of quartz, but simply to apply the known laws of rotatory polarization as they were first proved experimentally by Arago and Biot on this mineral. A quartz plate perpendicular to the principal axis rotates the plane of normally incident, plane polarized waves, through an angle which is proportional to the thickness of the quartz plate and also approximately proportional to the inverse square of the wave length used. The rotation effected by two superimposed plates is moreover the algebraic sum of the rotations produced by each separately.

By using, therefore, a properly constructed quartz wedge, it is possible to counteract exactly the effect, in plane polarized monochromatic light, of any crystal plate in any given position with respect to the nicols, by rotating the new planes of vibration, determined by the crystal plate back to the original plane of the nicols.

In the intensity formula (5),

$$I_1 = \cos^2 \phi - \sin 2\theta \sin 2(\theta - \phi) \sin^2 \frac{\pi}{\lambda} d (\gamma^1 - \alpha^1)$$

this rotation affects the angle θ only, and if the nicols be crossed, then

$$I_1 = - \sin^2 2\theta \sin^2 \frac{\pi}{\lambda} d (\gamma^1 - \alpha^1) \quad \text{Equation (11, page 359)}$$

In all measurements of extinction angles, however, θ is a small quantity and in place of the sine we may use the angle itself without sensible error; accordingly,

$$I_1 = 4K\theta^2. \tag{13}$$

This formula, which for small angles θ states that the light intensity is proportioned to the square of the angle θ, will be employed later in the description of a new combination quartz wedge for use in determining extinction angles.

In certain other methods, convergent polarized light is employed and the disturbing effects of an intervening crystal plate observed whose optic ellipsoidal axes are not precisely parallel with the planes of the nicols. The intensity formulae applying to such conditions are similar to those for plane polarized and the general deductions from the latter may be considered to apply to the phenomena in convergent polarized light. The methods involving convergent polarized light, however, have several important defects which render their general application cumbersome and unpractical.

In the foregoing pages, the intensity formulae for light transmitted by crystalline plates under different conditions have been developed and the attempt has been made to treat the subject in such a way that the results attained shall be directly applicable to the practical methods for determining extinction angles under the microscope. In the following sections, the different methods for accomplishing this end will be described, with special reference to their general applicability and relative accuracy, and the conclusions reached in this mathematical part will be used constantly as criteria of fundamental importance.

Methods.

Extinction angles can be measured either in plane polarized light or in convergent polarized light; and in plane polarized light the exact location of the positions of zero extinction is fixed, either by observing relative intensities of monochromatic light under special conditions or by means of the interference colors resulting from the use of white light. In all measurements of extinction angles it is imperative that careful attention be given to the source of light, especially if monochromatic light be used. The source should be as intense and steady and uniform as possible in order that the variation in the source of light itself be not mistaken for actual differences in the microscopic field. The rays of light incident on the preparation should, moreover, be as nearly parallel as it is possible to obtain them. To meet these requirements satisfactorily requires both time and patience, but in order to attain the best results they cannot be overlooked.

The microscope, moreover, should be in perfect adjustment, the optical system should be accurately centered and the cross hairs in the ocular should be precisely parallel with the principal planes of the crossed nicols. The adjustment of the microscope is not a difficult task to accomplish if suitable apparatus is at hand, and will be discussed briefly in part 2 of this paper.

Assuming the microscope to be in perfect adjustment and the source of light satisfactory, we may use any one of the following direct methods for measuring the extinction angle of a particular crystal plate:

Parallel Polarized Light.

(1) The ordinary method, which consists in turning the crystal plate under crossed nicols until the position of maximum

darkness is attained. This method is in general use and is equally well adapted for white light and for monochromatic light. With it any degree of accuracy can be attained provided a sufficient number of measurements be taken to reduce the probable error. In applying this method it is customary to note not only the positions of maximum darkness attained by the crystal when revolved clockwise from a position of bright illumination, but also when revolved counter clockwise from such position. This was the method used by Max Schuster* in his classic measurements of the extinction angles of plagioclase feldspars. He determined for each cleavage flake the position of zero extinction eighty times for clockwise revolutions of the plate and eighty times for counter clockwise revolutions, and averaged the two readings. His work in this line remains unsurpassed, even to the present time.

To increase the accuracy of each determination on a crystal plate under crossed nicols, different schemes have been devised, all of which depend on the disturbing influence of the plate on inserted plates or wedges of birefracting substances. Each of the inserted plates or wedges is constructed in such a way that the interference phenomena which it presents are markedly influenced by the slight disturbing effects from the crystal plate when it is not precisely in its position of zero extinction.

Sensitive Tint Plate.—Plates showing this interference color (violet of the second order) are usually made of selenite or quartz and are under certain conditions very sensitive to the slight changes which the crystal plate produces when it is not precisely in its position of total extinction. As a general rule, the eye is more sensitive to slight differences in color than in intensity, and in certain cases the sensitive tint plate can be used to advantage to increase the accuracy of the ordinary method. Its use is most effective on and practically limited to colorless plates showing low interference colors of the first order. Its efficiency is seriously impaired in the case of deeply colored minerals which veil the true interference color and also in thick plates of strongly birefracting minerals showing high interference colors, even red of the first order. It can, moreover, only be used with white light and accordingly cannot take cognizance of the dispersion of the bisectrices in the monoclinic and triclinic systems. This method is therefore not of general application and can be employed to advantage only under specially favorable conditions.

Bravais†*-Stöber*‡ *plate.*—This plate is also cut to show the sensitive violet interference color, and consists of two such

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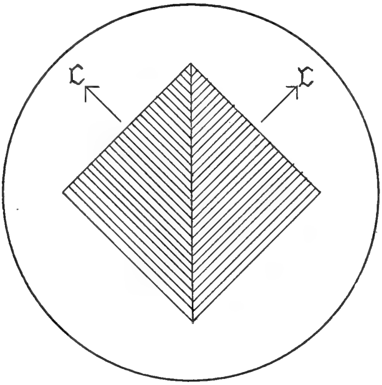
* Tschermak's Min. Petr. Mitth. v, 189, 1882.

† Comptes Rendus, xxxii, 113, 1851; also Pogg. Ann. xcvi, 397, 1855.

‡ Zeitschr. Kryst. xxix, 22-24, 1898.

plates in combination instead of a single one. A single sensitive tint plate of mica or quartz is taken and cut along a line at 45° with the directions of extinction; the one half is then turned through angle of 180° and the two halves recemented as indicated in the figure. By this combination plate, which is placed in the focal plane of the ocular, the interference color is made to fall in the one half and to rise an equal amount in the second, thus doubling the sensitiveness of the single plate.

Fig. 8.



This plate is intended for use only in white light, but under certain conditions it may serve to good advantage in monochromatic light.

*The Combination Wedge.**—On the principle of the Bravais-Stöber plate, the writer has had a combination wedge prepared in which the interference colors range from total darkness to green of the second order. This wedge was made by taking

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*This wedge was prepared with great care by Voigt & Hochgesang, Göttingen, Germany (cost, 48 mks.), and the writer desires to express his appreciation of the interest taken by the firm in the same. The compensation on different ends of the wedge, however, proved to be of unequal value, with the result that although the dark zero interference bands were precisely adjacent, the interference colors near the ends of the wedge did not coincide exactly. This defect could be eliminated by combining two quartz plates (45^{mm} long by 5^{mm} wide and of such a thickness as to show interference color green-yellow second order, the ellipsoidal axis $\mathfrak{c}$ of the one to be parallel to the long direction, while in the second $\mathfrak{a}$ is parallel), with two wedges of the same pitch (45^{mm} long by 5^{mm} wide and ranging in interference colors pale gray of the first order to violet gray at the top of the third order, and likewise the ellipsoidal axis $\mathfrak{c}$ parallel to the direction of elongation in one and $\mathfrak{a}$ to the same direction in the second); the wedge of long direction $\mathfrak{c}$ to be combined with the plate of long direction $\mathfrak{a}$. In this manner the plate and wedge compensate in the center of the wedge and the interference colors rise to about blue green of the second order at both ends.

an ordinary combination wedge* showing the zero interference band exactly in the center and green of the second order on each end, cutting the same longitudinally in half parallel to the ellipsoidal axes; the edges were then polished and the halves again recemented, the one half, however, having been rotated first through 180°, so that in the resultant combination by wedge the phase difference of the adjacent half at any point of insertion is always equal and opposite. By this method the principle of the Bravais-Stöber plate is extended to cover interference colors from total darkness to blue green of the second order, and to allow the observer to select an interference color which, in combination with that of the mineral plate examined, is most sensitive. The low gray tints of this wedge (particularly the dark band region on both sides of which the interference colors rise and thus divide the field into four quadrants and produce an effect similar to that of the Bertrand ocular) have been found specially useful with minerals showing interference colors from red first order to blue second order. This wedge is held in a brass carriage, which in turn slides in the wedge holder shown in fig. 10, and is viewed by the Ramsden ocular.

Calderon† *Calcite plate.*—This plate is also placed in the focal plane of the ocular and consists of two calcite plates placed side by side and so cut that the direction of extinction in each plate makes an angle of about 3½° on opposite sides of the common line of junction. The plate is so thick that the interference color is white of the higher orders and when used alone without intervening crystal plate, lights the entire field under crossed nicols with a dull gray tone. If a crystal plate whose lines of extinction do not coincide with the principal nicol planes be then observed, the field appears divided into two unequally illuminated halves and only when the extinction directions coincide with the nicol planes is the intensity of illumination in both halves equal. Calderon claims an accuracy of ±2′ with this ocular, but for a single determination and for general preparations the probable error is considerably larger

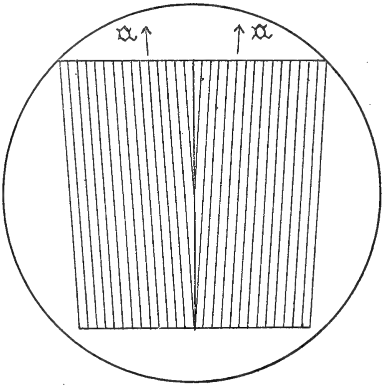
* Compare F. E. Wright, Tschermak's Min. Petr. Mitth. xx, 233-306, 1901; also Jour. Geol., 33-35, 1902.

† Zeitschr. Kryst., ii, 70, 1878.—The calcite twin plates of a Calderon ocular from R. Fuess in Steglitz were tested by the writer and found to be inaccurately ground. The plate was 3·18^{mm} thick and cut at an angle of about 45° with optic axis. The extinction angle in each half of the plate was measured in convergent polarized light by means of the dark bar in the center of the field and found to be + 4·4° on the one half and 3·2° on the other. Extinction angles measured with this ocular, using the junction line of the plate as the line of reference, would therefore be out 0·6° from this source alone. The field of the ocular is, moreover, small and unfavorably lighted because of the thickness of the plate and of the wide dark junction line across the center of the field, which in turn disturbs the exact matching of the halves of the field.

(10′–15′). The principle on which this method is based is evident from the intensity formula, for in case the ellipsoidal axes of the plate do not coincide precisely with the principal nicol planes, they make unequal angles with the optic ellipsoidal axes of the calcite (in the one half, this angle is $3\frac{1}{2}^\circ + \theta$ and for the second $3\frac{1}{2}^\circ - \theta$) and this produces at once a marked difference in intensity of illumination.

Quarter-undulation plate of H. Traube.†—This plate consists of two adjacent quarter-undulation mica plates so cut that

FIG. 9.



the optic axial plane of each includes an angle $3\frac{1}{2}^\circ$ with the common line of junction and for slight deviations of a crystal plate from its true position of extinction, the two halves appear unequally lighted, and only when the crystal is precisely in its position of zero extinction do the halves show the same intensity of illumination.

Twinned Selenite plate.—The use of a twinned selenite plate has been recommended recently by E. Sommerfeldt† for the accurate adjustment of the ocular crosshairs to the planes of the nicols. But the same twins can be made to serve admirably in the measurement of extinction angles. The extinction angle which the ellipsoidal axis makes in each plate with the twinning plane is $37\frac{1}{2}^\circ$, and if the twinning line on such a plate be turned to the diagonal position with the crossed nicols, the extinction angle on each side of the nicol measures $45^\circ - 37\frac{1}{2} = 7\frac{1}{2}^\circ$, but in the opposite halves different optic ellipsoidal axes are adjacent the principal nicol plane. The net result of this arrangement is a change in intensity dependent not only on

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[*] Neues Jahrbuch, 1898, i, 251.

[†] Zeitschr. f. wissensch. Mikroskopie, xxiv, 24–25, 1907.

FIG. 10.

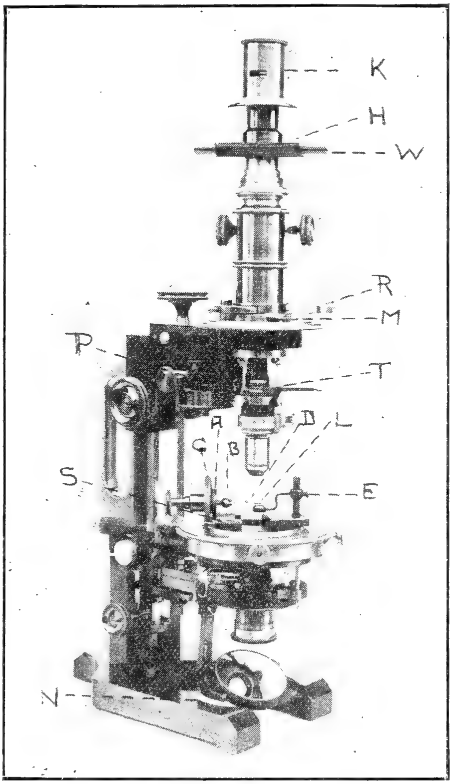

FIG. 10.—Mikroskop-polymeter of Voigt and Hochgesang carrying wedge holder H and also device described below for holding small crystals. The wedge holder in turn carries a cap nicol, K, and a Ramsden ocular in the focal plane of which the wedge, W, is introduced. The crystal-holding device consists of the following parts: S, the stand; C, graduated vertical circle with 1° divisions: A, centering plate; B, ball and socket adjusting device; D, crystal holder; L, plano-concave lens for holding drop of liquid of same refractive index as crystal and held by stand, E.

The mikroskop-polymeter is a useful instrument in many ways but for accurate work the mechanical workmanship on the same leaves much to be desired. The fine adjustment screw is practically worthless for even approximate readings, the accurate adjustment of the different circles to the common optic axis is not possible, and even if once accomplished does not remain in adjustment: the divisions on the different verniers are inaccurate; many other defects have been felt by the writer and several of them remedied in the workshop of the Geophysical Laboratory.—A stop diaphragm M has been introduced into the upper tube, also an optic axial angle reflector, R (compare F. E. Wright, this Jour., xxii, 19-20, 1906); a holder for the combination wedge is shown at T, which fits on the objective supporting arm and is revolvable about the axis, an arrangement which has proved advantageous in place of revolving the microscope stage when the interference plates are inserted.—The fine adjustment screw P has been lengthened so that it can be reached from either side of the microscope. The base of the stand at N has been milled out to allow space for the reflector when the condenser lens is lowered.

the angle but also on the different compensations of the path differences in the two plates, and if white light be used this results in a rapid change in interference color in the two halves if the crystal be only a small angular distance from its position of true extinction.

The writer has had such a plate cut showing the sensitive tint and also a wedge, so that on insertion different interference colors, or intensities in monochromatic light, can be used for which the eye under certain conditions is most sensitive. These plates, as well as the preceding, are inserted in the focal plane of the objective and the junction line serves for the vertical crosshair. For such plates the Ramsden positive ocular has been found by experience to be best suited and a specially constructed holder convenient.

Artificially twinned Quartz plate.—Still another advantageous arrangement can be had by cutting on a polished quartz plate parallel to the principal axis a vertical edge making an angle of about 3°–6° with the principal axis. The quartz plate is then divided transversely to the polished edge and the polished edges cemented together, thus producing an artificial twin whose two halves extinguish at equal and opposite angles from the common line of junction. Such plates may then be ground to a thin plate showing either the sensitive tint or dull gray of the first order or to wedge form, thus increasing the range and usefulness of the device.

All of the preceding plates, the Bravais-Stöber, the Calderon and the Traube, the selenite twin plate and the quartz combination plate wedges of the last paragraph, can be made somewhat more sensitive by dividing the field into quadrants instead of halves, after the example of Bertrand in his rotatory polarizing quartz plates described below.

Bi-nicol ocular.—In the practical application of these different types of plates the angle θ has been small $(2-4°)$ and found to furnish good results, but in each case there is a particular angle θ which is best adapted for the observations; the limit of sensitiveness of different eyes introduces, moreover, a variable element of such wide range that the angle θ cannot be calculated and fixed once for all. In order therefore to have control over all angles θ and thus in each instance to be in position to procure the best possible conditions, the writer has had constructed the following ocular attachment.

The principle of construction of the apparatus is apparent from the figure, and need not be expressed at length at this point. The light after passing through the lower nicol and the crystal plate reaches the lower reflecting prism pair of this ocular and passes thence through appropriate nicol prisms (Thompson prisms) or birefracting plates of exactly the same character, and after total reflection in the upper prism pair is again brought back to the common field of vision and viewed by the Ramsden ocular and upper nicol. The nicol prisms or birefracting plates fit in collars and can simultaneously be revolved about the axis and in opposite directions so that the angle θ can be made to vary from $+90°$ to $-90°$ in each plate and at any instant θ of the first plate is equal and opposite to θ of the second plate. In the mechanical construction of this apparatus, special care has been taken to make the angular movements of both plates exactly equal and opposite.

Fig. 11.

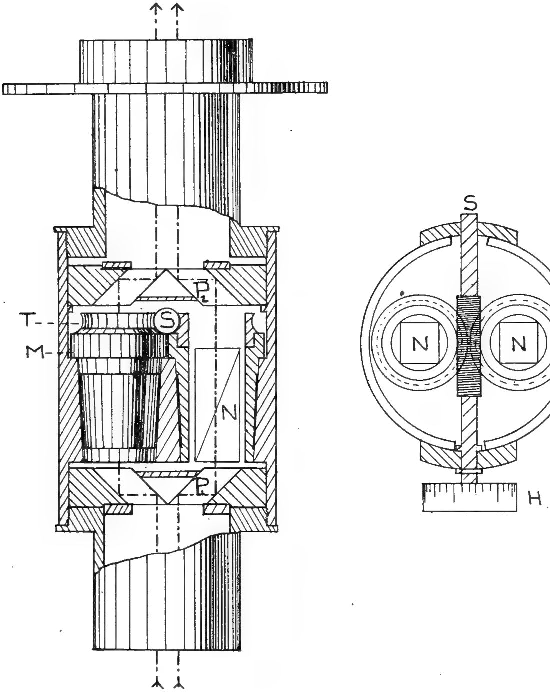

Fig. 11.—Bi-nicol ocular; consists of the following parts: Two pairs of reflecting prisms, P_1 and P_2, (ground specially for the purpose by Steeg & Reuter of Homburg v. d. Höhe, Germany); two tapering revolving brass holders, M, into which either two Thompson prisms, N, or birefracting plates are introduced. These conical brass carriages are revolved in opposite directions and through equal angles by means of the worm thread S and grooved wheels T, the angle of revolution being read off directly on the head H. The bi-nicol ocular fits in the microscope as an ordinary ocular and into it in turn a Ramsden ocular is introduced and above this the cap nicol.

With this revolving bi-nicol ocular, it is thus possible to allow any proportion of the light incident on the crystal plate to pass through the upper nicols by simply revolving the same and at every instant to state what percentage is passing through. The particular angle of revolution θ for which the intensity of light transmitted is best suited for the maximum sensitiveness of the eye of the observer can be readily ascertained, and the actual position of extinction for any given mineral plate be determined by its use. By means of the bi-nicol ocular, the adjustment of two crossed nicol prisms can also be tested accurately and easily.

This ocular, although serviceable, suffers from one defect which it is difficult to overcome satisfactorily, namely, the depolarizing of the total reflecting prism pairs on light waves transmitted when the planes of the revolving nicols are not parallel with the planes of the polarizer and analyzer. As a result a certain amount of false light is introduced into the field and tends to veil the sharp contrast of the two halves and thus to decrease the sensitiveness of the instrument.

Bertrand plate—In place of birefracting plates, which introduce an entirely new set of conditions in the path of light waves and which complicate the expression for the relative intensity correspondingly, Klein* and Bertrand† have used the rotary power of quartz plates, cut normal to the principal axis, on the plane of polarization of normally incident, plane polarized waves. As shown above, the total effect of such a quartz plate in monochromatic light is merely to increase the angular distance θ in the intensity formula (6). This power of rotation of quartz varies with different wave lengths and with the thickness of the plate. If white light be used, interference colors result.

A quartz plate $7\cdot50^{mm}$ thick shows the sensitive tint under crossed nicols and can be used to good advantage in measuring extinction angles, since for slight deviations of the crystal plate from the position of true extinction its interference color rises or falls. To increase its sensitiveness, Bertrand combined two plates (2^{mm} in thickness) of right-handed with two plates of left-handed quartz, so that each right-handed plate is adjacent to a left-handed plate. This plate is inserted in the focal plane of the ocular and the sharp junction lines serve as crosshairs. The Bertrand plate can be used in monochromatic light, provided for the particular wave length used, its angle of rotation is not a multiple of π, in which case darkness ensues and the observed effect is nil. By revolving the upper nicol it is possible in white light to bring out the sensitive interference tint over the entire field covered by the Bertrand plate, and in such a position a very slight turn of an intervening crystal from its position of true extinction is sufficient to disturb this equality

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* Neues Jahrbuch, 1874, p. 9.

† Zeitschr. Kryst., i, 69, 1877.

of interference color and to divide the field into four quadrants, the opposite sections of which are similarly colored, while adjacent sections are differently colored.

The Bertrand plate is best adapted for use in white light, although it is possible to use it in monochromatic light provided its thickness be correct for the particular wave length employed.

The quartz half shade plate of S. Nakamura.—In a recent paper,* S. Nakamura discussed the problem of the sensitiveness of the half shade system and arrived at practically the same conclusions as those noted above. He suggests the use of a double quartz plate of $\cdot 4^{mm}$ thickness instead of $3\cdot 5^{mm}$ or 7^{mm} thick as in the Bertrand ocular, and by actual tests finds the theoretical deductions valid and the plate useful. The thickness of $\cdot 4^{mm}$ is equivalent to an angle $(90-\phi)$ of about 8·67° on each side of the junction line; under certain conditions of illumination this angle is undoubtedly the best, and with the plate the accuracy of the measurements thereby attained equal to that of any of the other measuring devices.

Bi-quartz wedge-plate.—It is possible, however, to construct a combination wedge of quartz plates of such a character that any angle of rotation from 0° to any other value, positive or negative, can be had on insertion of the wedge, thus adapting to wedge form the advantage of the revolving bi-nicol ocular. This has been accomplished by combining two plates of quartz cut normal to an axis and of specified thickness, the one of right-handed, the other of left-handed quartz, each with a wedge of quartz of the opposite sign of rotary polarization, as indicated in figure 12.†

The effect of this combination is to produce zero rotation in each half wedge where plate and wedge have the same thickness and as the wedge is inserted or drawn out from this point of zero rotation the angle of rotation increases proportionately and in a positive sense on one side of the junction line of the combination and in a negative sense on the opposite half. This combination wedge, which is introduced at the focal plane of the ocular, divides the field under crossed nicols into two halves, the intensity of color of which at any instant is equal, provided no intervening crystal plate is present or is rendered inactive

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* Centralblatt f. Mineralogie, 1905, 267–279. Compare also J. Macé de Lépinay, Jour. de Phys. (2), iv, 267, 1885; (3), ix, 585, 1900. Unfortunately this paper did not come to notice until after the manuscript of the present article had been sent to the press and the mathematical discussion by S. Nakamura, which considers the problem from a somewhat different standpoint, could not well receive the analysis and recognition which otherwise might have been given it in the general theoretical part.

† Made for the writer by Steeg & Reuter of Homburg v. d. Höhe, Germany. Cost, 100 marks. The accuracy of this wedge was tested by the writer and the grinding found to be exceptionally perfect.

by the parallelism of its ellipsoidal axis with the principal planes of the nicols. So soon as the crystal is turned even a very small angle out of this position, the intensity of illumination of the two fields is no longer equal. By inserting or withdrawing the combination wedge, the most advantageous angle of rotation in the two fields can be procured so that the difference in intensity between the two halves is most apparent. In effect this wedge is identical with that of the bi-nicol ocular described above, is much simpler in construction, and requires no adjustment; the one condition which must be fulfilled for satisfactory results is that the wedge be not tilted on insertion but that the optic axis remain always parallel with the optic axis of the microscope, otherwise disturbing birefringence phenomena appear. The wedge carriage should, therefore, slide in an accurately fitting holder such as

Fig. 12.

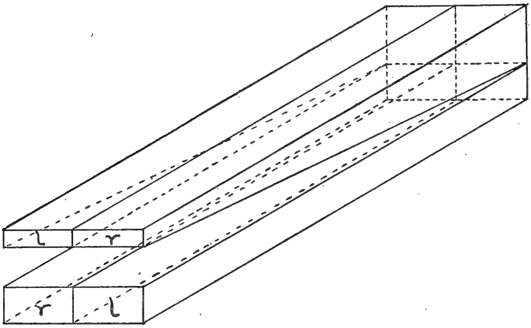

Fig. 12. Bi-quartz wedge-plate. In the plate-wedge ground for the writer the two quartz plates are 35$^{\text{mm}}$ long, 6$^{\text{mm}}$ wide, and ·35$^{\text{mm}}$ thick. The wedges are ·3$^{\text{mm}}$ thick at the one end and ·5$^{\text{mm}}$ at the thick edge. Cementing material is Canada balsam whose refractive index is 1·54, while ω for quartz is 1.544, a difference so slight as to render inappreciable the exceedingly slight deviation of the waves caused by the slight wedge surface of the wedge. This inclined surface is mounted next the Canada balsam and care is taken by inserting a thin glass strip at the thin end to make the upper and under surfaces of the completed wedge parallel. The thickness of the wedge is ·9$^{\text{mm}}$. At the one end the rotation is ±1·1°; at the thick end, ±3·2° for sodium light, while at ·85$^{\text{mm}}$ from the thin edge the rotation is zero in both halves. For a wedge-plate of an angle of rotation 0° to 10° the following specifications are suitable: length 50$^{\text{mm}}$, width of each half 6$^{\text{mm}}$, total width of wedge 12$^{\text{mm}}$.; thickness of plate, ·4$^{\text{mm}}$; thickness of wedge at thin end ·35$^{\text{mm}}$; at thick end, ·85$^{\text{mm}}$. In such a wedge the point of zero rotation is 5$^{\text{mm}}$ from the thin end. At the thin end the rotation is ±1·1°; at the thick end, ±9·9°. In the article following this, specifications for a wedge with rotation of 15° at the thick end are given. In preparing the wedge it is necessary that the edges be ground and polished in order that the central division line (fig. 11) be as sharp as possible. The two halves are eventually cemented side by side with Canada balsam and any disturbing influence thus eliminated which might arise from total reflexion on the sides.

shown in fig. 10 above, which was constructed in the workshop of the Geophysical Laboratory.

Methods involving revolution of upper nicol.—In all of the preceding methods the nicols have been considered crossed and the crystal plate revolved. The intensity formula shows, however, that the relative intensity is dependent not only on the angle θ of the crystal plate but also on ϕ, the angle between the principal planes of the nicols. It was shown in the general mathematical treatment that this method is in general at least twice as sensitive as the method based on the revolution of the crystal plate under crossed nicols. The mode of application of this method to any particular crystal plate is obvious and consists simply in placing the crystal under crossed nicols in its position of apparent true extinction and then observing, either in white or monochromatic light, the changes which occur on revolving the upper or lower nicol through small angles with its normal position. In case the crystal is actually in its position of true extinction, the crystal and field attain their position of maximum darkness simultaneously and show the same increase in its intensity of illumination; if, however, the crystal be not in its position of true extinction, but a small + angle, as 30′ distant, then for a position of the nicol +2° from its normal position, the crystal plate will appear lighter than the field; and vice versa for the nicol −2° from its normal position the crystal plate will appear darker than the field. This method is extremely simple in manipulation and does not require special apparatus, but seems not to have been applied before to the measurement of extinction angles. Weinschenk,* in describing the adjustment of the nicols in the microscope, uses the interference phenomena which occur under these conditions, but does not appear to have applied conversely the principle to the practical determination of the optic ellipsoidal axis in a given crystal plate.

To double the sensitiveness of this method of revolving the upper nicol, the bi-nicol ocular attachment of fig. 11 can be used. By this device alone, without the upper nicol used in the above methods, the two halves of the field in the ocular preserve the same intensity of illumination at every instant, provided no disturbing crystal plate intervenes. If the position of the latter does not coincide precisely with its true position of zero extinction, the two halves of the field appear unequally illuminated and by revolving the nicols that position of the nicols can be found for which the effect is most pronounced for a given angle θ.

In its effect the bi-quartz wedge plate is identical with the revolving bi-nicol scheme, and has the advantage of requiring

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* Zeitschr. Krystall. xxiv, 581-583, 1895.

no adjustment and of not suffering from the false light of depolarization noted above.

Convergent polarized light.—Two methods have been proposed which require convergent polarized light and are based on the change in aspect of symmetrical interference figures caused by the intervening crystal plate when it is not precisely in the position of zero extinction. The idea underlying the methods is that the eye can detect more readily slight changes in the shape of a symmetrical interference figure than proportionate changes in intensity or color. Theoretically, this principle is excellent, but its practical application to mineral sections is less satisfactory. The first method of this type was proposed by Kobell in 1851, who used a plate of calcite normal to the optic axis as his test plate. The microscope was arranged for convergent polarized light and the crystal plate with the calcite test plate above it placed on the microscope stage and turned until the interference figure appeared perfectly normal and undistorted. Practically, the following objections apply to this method. The optical system of the miscroscope requires changing each time to meet the new conditions; during the observations the crystal itself is lost sight of, and in the case of minute crystals or crystals with undulatory extinction this is a serious drawback. Moreover it is tacitly assumed that in the crystal plate itself for directions other than the normal to its surface of the crystal plate the planes of polarization remain parallel, which in general is only approximately true even for small fields which include only a small angle with the normal.

In the Brezina† method a more complicated interference figure is produced by two calcite plates cut at a small angle with the optic axis and cemented together one above the other in such a way that the optic axes of the two are in the same plane and at equal angles with the normal. The interference figure from such a combination is noteworthy because of a dark vertical bar through the center of the field. A slight revolution of an intervening crystal plate displaces this bar noticeably, but the same objections noted in the Kobell method apply with equal force to this method, with the result that neither method is made use of at the present time by working petrologists. In fact, both these methods were suggested before the petrographic microscope had been introduced.

The relative sensitiveness of the different methods.—The term position of extinction means practically that position of a birefracting plate for which light waves are transmitted without changing their plane of polarization and for which no light

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* Pogg. Ann., xcv, 320, 1855.

† Described in Schrauf's Lehrb. d. Phys. Min. ii, 219-220, 1868.

passes the upper nicol, i. e., the field is just as dark as though no crystal plate were there. A revolution of the plate through a very small angle from its position of true extinction allows an equally small percentage of the total amount of incident light through the upper nicol and the field is very dimly illuminated. For a given angle of revolution, the actual amount of transmitted light can be increased only by increasing the original source of light. Since, however, it is not possible to increase the intensity of such a source indefinitely, and the human eye is sensitive only to a certain limit, the position of actual extinction can only be determined within a definite degree of exactness. By means of the above devices, however, certain phenomena are introduced which increase the accuracy of such a determination, even though the field of original illumination remains the same. That method or device is obviously the best for which the probable error of a single determination under the same conditions is the least.

In comparing the relative accuracy of the methods described above it will facilitate the presentation to assume definite conditions and then by means of the theoretical intensity curves (figs. 2–7) to test the results attainable by the different methods under the most favorable conditions.

Let it be assumed that under the conditions of experiment the eye of the observer is of such sensitiveness that he is able to detect ·05 of one per cent of the total light intensity; in other words, he can just detect the difference between the dark field of the microrcope under crossed nicols and a crystal section turned at such an angle as to allow ·05 of one per cent of the total intensity through the upper nicol. For all positions of the crystal, then, for which the intensity of the emergent light is less than ·05 per cent, the crystal will appear absolutely dark. The heavy curves in figs. 3–7 indicate the relative intensity of illumination of a crystal under crossed nicols for all positions of its major ellipsoidal axis from 88° to 92° or −2° to +2° with the plane of the polarizer; in fig. 3 there is an interval of 38′ at least on each side of the true extinction position for which the eye is unable to detect any interference illumination. The possible error on a single determination under the most favorable conditions is in this case at least ± 38′ while for fig. 4 it is ± 44′; for fig. 5 ($K=\frac{1}{2}$) ± 55′; for fig. 6 ± 1° 17′; while for the $K = 0$ the crystal is dark for all positions. In any crystal, therefore, the conditions are most favorable when the plate is of such thickness that $K = 1$ or the emergent waves are half a wave length apart (in opposite phase). Conversely, having given a crystal plate, not all wave lengths are best adapted for extinction-angle measurements. If yellow sodium light be used, a plate showing the sensitive violet interference tint is worthless since for that tint the path difference is 572 $\mu\mu$, nearly a whole wave length of Na light (589$\mu\mu$), and for this difference $K = 0$ and fig. 7 applies. If sodium light be used, then plates should be chosen for which the phase difference of the two emerging waves is $\frac{(n+1)\lambda}{2}$, bright yellow of the first order or pure yellow of the second order or green yellow of the third order, etc. This is an important consideration and applies to all methods involving the intensity equations.

The visible spectrum includes wave lengths ranging from about 400$\mu\mu$, and 700$\mu\mu$, the interference color in white light ranges from about red of the first order to blue of the second order; in short, the sensitive interference tint region of the Newton color scale as determined by G. Quincke.* For this interval the distance between the emergent waves is not far from a whole wave length for the major part of the visible spectrum; in other words, the phase difference is such that K is a small fraction not greatly different from zero and the intensity curves for practically all wave lengths will be covered by 5–7. These are, however, the least favorable for showing difference in intensity and such plates are, therefore, the least suitable for the measurement of extinction angles by methods based on intensity differences. On the other hand, plates showing interference colors gray to yellow of the first order are best suited for such measurements. If the methods involving interference tints be used, however, these objections do not hold with equal force. Experience has shown that in case the mineral plate does show red or blue interference tints of the first and second orders the best determinations can be made either by the method of revolving the upper nicol or by the bi-quartz wedge plate, and the true position fixed by noting the absence of abnormal interference colors on revolving the nicol very slightly or inserting the wedge.

After this digression on the most suitable sections for the measurement of extinction angles, fig. 3 may again be considered and the relative accuracy of the different methods under the same conditions of experiment deduced.

The heavy curve indicates that for the assumed limit of sensitiveness ·05 per cent of the total intensity, an error of at least ±38′ on a single determination is possible by revolving the crystal plate alone under crossed nicols. On the other hand, if the crystal plate remains stationary and the upper nicol alone is revolved, the other intensity curves of fig. 3 are valid, each curve indicating the intensity of illumination of

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* Pogg. Ann., cxxix, 177, 1866.

the crystal plate for a specified angular distance from its position of true extinction during the revolution of the upper nicol from 88° to 92°. These curves indicate that the probable error with this method is less than half as great as in the preceding method, for if the crystal be only ±15′ distant from its position of true extinction, differences in intensity can even then be detected on revolving the upper nicol.

The changes in intensity of illumination of the microscopic field on revolution of the analyzer are indicated by the 0′ curve, while for the crystal plate the 15′ curve is applicable. At 88° 43′ (fig. 3) the field is just beginning to show detectable illumination (·05 per cent of total intensity), while for the same angle the crystal is illuminated with 0·97 per cent of the total intensity, nearly twice as great and easily noticeable. In this position the crystal plate appears, therefore, decidedly lighter than the field. On the other side of 90° the crystal plate passes its limit of light sensibility under the assumed conditions at 91° 42′, while for the same angle the microscopic field is illuminated by ·97 per cent of the total intensity; in this case the field is appreciably brighter than the crystal and the difference can be readily detected by the eye.

If white light be used, these differences are accentuated by the abnormal interference colors which appear in the crystal plate when it is not precisely in the position of true extinction. This method of revolving the upper nicol has the advantage, furthermore, of not being dependent on the accuracy with which the nicols are crossed, since all data are referred at once to the plane of the analyzer. It is not, however, so advantageous in very weakly birefracting or deeply colored mineral plates.

The sensitiveness of the latter method can, moreover, be doubled by devices which allow the phenomena on both sides of the 90° position to be observed simultaneously. This is the end striven for in the ocular plate, the Bravais-Stöber plate, the Calderon plate, the Traube plate, and accomplished most effectively by the new circularly polarizing bi-quartz wedge and also by the bi-nicol ocular, though less satisfactorily. In each of these last two devices the plane of polarization of the incident waves is turned through equal angles on both sides of the junction line of the two parts, so that the field appears equally lighted throughout, while if the crystal plate be not in its position of true extinction, it will appear lighter than the field in the one half and darker in the second. Since, however, there is an angle best suited under the given conditions to show these differences most clearly, it follows that the best results can be had with a plate or apparatus in which the angle ϕ can be varied at will. This is true of both the circularly polarizing wedge plate and the bi-nicol ocular, and by their use the probable error of the extinction position of any crystal plate is at least one-fourth that of a determination after the usual method by revolving the crystal plate under crossed nicols. Experience has shown that with favorable sections, extinction angles can be determined by the use of the bi-quartz wedge with a probable error of less than $\pm 10'$ on a single trial.

Still another method for obtaining the most favorable conditions of experiment with a given plate is that suggested on page 374 with the artificially twinned quartz wedge. The two halves of this wedge extinguish at a small angle (as 3°) on opposite sides of the line of junction, and by inserting the wedge that particular interference color, or phase difference if monochromatic light be employed, can be produced for which the given angle of revolution (3°) is the best. This wedge, however, is less favorable than the circularly polarizing bi-quartz wedge, since its twinning line must be inserted precisely parallel with the plane of the polarizer, while with the circularly polarizing bi-quartz wedge the rotation of the planes of polarization of transmitted waves is entirely independent of the line of junction of the adjacent halves.

In the preceding pages, special emphasis has been placed on those methods for measuring extinction angles which are of general application and which are based on intensity differences. The other methods, which are of limited application, and can be used only in white light on favorable sections, depend on differences in interference colors produced by slight deviations of the crystal plate from its position of true extinction. Although these methods are serviceable in many instances, their application and the results obtained thereby are so dependent on the conditions of experiment that they are difficult to treat satisfactorily in a general way. Experience has shown that they are not more sensitive than the other methods and usually much less so. This is true both of the selenite sensitive tint plate and of all combinations of the same.

Experimental Tests.—To test the different methods under different conditions, different mineral plates were chosen and the position of true extinction on each determined by the different methods under precisely the same conditions of illumination with white light.—On an anhydrite plate showing white interference tints of the higher orders the possible error of a single determination by revolving the crystal plate under crossed nicols was found to be about 1·1°; by revolving the upper nicol alone, ·4°; by inserting the quartz wedge, about 0·1°; by using the Calderon ocular, about ·5°; by means of the Bertrand ocular, about 0·1°; with such a plate the sensitive tint plate is of no value since the interference color of the anhydrite plate itself is so high that the violet of the inserted plate has no effect and the differences in intensity which occur, do so in a strongly lighted field and are not easily discernible.—Similar measurements were made on an apatite plate parallel to 10$\bar{1}$0 and showing the interference tint, red of the first order. The possible error of a single determination of the position of true extinction on turning the crystal plate alone under crossed nicols was found to be ±·9°; on revolving upper nicol about ·2°, accurate because of abnormal interference colors which appear when the plate is distant only a slight distance from its correct extinction position; on inserting the bi-quartz wedge plate 0·2° to 0·3°; with the Calderon ocular, about 0·3°; with the Bertrand ocular, about 0·3°; the sensitive tint plate is again of no value since the interference color changes comparatively slowly as crystal is revolved.—A section of nephelite parallel to 10$\bar{1}$0 and showing the interference color, yellow first order, gave the following results: On revolving the crystal plate alone, possible error ·4°; on rotating upper nicol, less than 0·1°; with bi-quartz wedge less than 0·1°; Calderon ocular about 0·2°; Bertrand ocular less than 0·1°; sensitive violet plate still of very little value as a method; only slight changes in color for large angles of revolution of plate. On a plate of colorless gehlenite of very low interference color, dull gray, first order, the sensitive tint plate proved as satisfactory as any other and more so than the method of turning the crystal plate under crossed nicols or of revolving the upper nicol or the Calderon ocular. The Bertrand ocular and the bi-quartz wedge plate proved about as favorable, the probable error being slightly less than 0·5°.—A plate of strongly pleochroic tourmaline was also used and the following results obtained: Probable error of determination on revolving crystal plate alone, about 1·6°; the method of revolving upper nicol is of little value because of deep natural color of mineral and consequent inability to match fields; with the bi-quartz wedge plate 0·3°; Calderon ocular, about 0·4°; Bertrand ocular, about 0·5°. The sensitive tint plate is useless because of strong natural color of mineral which veils the true interference colors.

The results of these tests show that the theoretical deductions from the general equations are in general valid, but that in certain instances other factors, as natural color and very low birefringence, become dominant and tend to render some of the methods less sensitive and to favor the use of other, in general less suitable methods. The bi-quartz wedge plate, however, seems to apply in all cases with equally favorable results and to equal in sensitiveness any of the methods, whether of local or of general application.

2. *The Adjustment of the Petrographic Microscope with Special Reference to the Measurement of Extinction Angles.*

A petrographic microscope in perfect adjustment should satisfy the following requirements: (1) Its optical system should be accurately centered; (2) the axes of revolution of all revolvable parts, whether stage or ocular, should coincide with the optic axis of the microscope; (3) the principal planes of the nicols when crossed should be precisely 90° apart; (4) the crosshairs of the ocular should be parallel with the principal planes of the nicols. Of the four conditions, the first two can be accomplished without difficulty, and with the adjustment screws fitted on every petrographic microscope. The last two, however, require special appliances for accurate adjustment, and without these can be effected only with difficulty.

The test usually applied in ascertaining the correct position for crossed nicols is that of the Bertrand ocular. A cap nicol is used over the ocular and turned until the field of the Bertrand ocular shows uniform intensity of illumination throughout. This can be accomplished readily and with an error of less than ±15′ if strong illumination be used. The cap nicol is then revolved through an angle of 90°, the lower nicol removed in its carriage, the upper nicol inserted and tested by the cap nicol in its new position and adjusted until it is actually crossed. The Bertrand ocular, however, furnishes only one angle of rotation for the emerging waves, and allows of no variability in this angle to meet different conditions in the best way possible. This can be accomplished, however, by use of the circularly polarizing bi-quartz wedge plate described above or the bi-nicol ocular. With the bi-quartz wedge plate the cap nicol is unnecessary and crossing of the microscope nicols can be tested directly. For this purpose, parallel light should be used and the entire lens system, both condensor lenses, objective and ocular, removed from the microscope; parallel incident rays are then allowed to fall on the reflector of the microscope (either sun rays or strong white light or the rays from a Nernst filament or arc light emerging at the focal point of a large lens). The parallelism of the incident rays is necessary and an important factor, since with the thick quartz plates a slight deviation from normally incident and parallel light produces disturbing interference phenomena. The bi-quartz wedge-plate in its metal casing may then be placed on the microscope stage and with it the accuracy of the crossing of the nicols tested directly, just as the position of zero extinction of a mineral plate is tested. The error of such a determination should be considerably less than 10′ of arc.

The final step in the adjustment is the alignment of the crosshairs of the ocular with the principal planes of the nicols. Many methods have been suggested for this purpose which may be used to advantage. A mineral showing good cleavage or lines of growth and parallel extinction (flakes of anhydrite or crystallites of quartz) serve well for the purpose. These are first placed in the position of zero extinction (determined accurately by means of bi-quartz wedge plate), and the crosshairs of the ocular brought to parallelism with the crystal edge or cleavage line. The chief difficulty in this method lies in the fact that it is exceedingly difficult to obtain suitable material.

E. Sommerfeldt* has recently suggested the use of a twinned plate of selenite of sensitive tint. The plate is turned until under crossed nicols the interference colors in the two halves are of precisely the same tint, in which position the twinning line parallels the principal planes of the nicols. This method is sensitive and satisfactory, especially if, instead of a plate, a wedge of the material be used, with which the interference color can be changed until that particular tint, for which the observer's eye is most sensitive, covers the field. In this connection care should be taken to select a selenite plate in which the twinning line is perfectly straight. In the selenite plate, however, the angle which the adjacent ellipsoidal axis in each half makes with the twinning line is 37½°, a very large angle and not so well adapted to show slight deviations from the true position as a twin of smaller symmetrical angle. In this connection experiments with plagioclase lamellæ were tried but abandoned, since it was found by experience to be exceedingly difficult to procure suitable material for the purpose; a simpler method can, however, be used, which accomplishes the same purpose more readily. On a thin plate of quartz, cut parallel to the principal axis, an edge surface, making an angle of 4°–6° with the principal axis, is first ground and polished. The plate is then cut in half at right angles with the polished edge surface and the two halves placed with their polished edges side by side and cemented with canada balsam, thus producing an artificial twin of any angle which may be selected as most suitable and best adapted for fixing the crosshair in the ocular. The twin is finally ground thin and polished either to the sensitive tint or a pale gray of the first order or in wedge form.† Like the selenite twin plate, it is placed on the stage of the microscope and revolved under

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* Zeitschr. für wissenschaftliche Mikroskopie, xxiv, 24–25, 1907.

† Such a plate and also wedge were prepared for the writer by Voigt & Hochgesang of Göttingen, and have proved satisfactory in every respect. The twinned selenite plate of sensitive tint cost 5 marks; the wedge (I–III order interference colors), 21 marks.

crossed nicols until its halves show equal intensity of illumination, in which position the line of junction fixes the direction for one of the crosshairs of the ocular.

By use of the bi-quartz wedge plate and the artificial quartz twin plate or wedge, the adjustment of the nicols and also of the crosshairs in the ocular is a matter of only a few moments, and the method followed is theoretically and practically more accurate than the other methods for adjustment which have been suggested.

3. A Device for Holding Small Crystals for the Purpose of Measuring Extinction Angles in Zones; also for Measuring the Optic Axial Angle of such Fragments directly.

In measuring the extinction angles of certain minute artificial pyroxene and other crystals in the prism zone, the writer has had occasion to use the following holding device or finger, which has proved both convenient and practical.* (Fig. 10 on stage of microscope.)

As indicated in the figure, it consists of two parts, a holding or clamp device for the crystal itself, and a universal ball and socket joint and centering plate for adjusting and centering the crystal, and a vertical circle for reading any specified angle of revolution of the crystal. A small crystal ($1–2^{mm}$ in length) thus held and adjusted is immersed in a drop of liquid of the same refractive index and thus the disturbing phenomena of refraction and total reflection eliminated. The liquid drop is contained in the concave side of a planoconcave lens of 6^{mm} diameter (ground for the purpose by the Scientific Shop of Chicago), which in turn is held by an adjustable and supporting arm.

In work with artificial preparations particularly it is often desirable to measure extinction angles on certain minute faces, or optical axial angles, of small fragments too minute for the optic axial angle apparatus and not suitable for measurement by one of the microscopic methods,† and this device has been made to fill that want. After adjustment and immersion in a liquid of refractive index β the optic axial angle can be read off directly on the vertical circle of this apparatus.

Summary.

The measurement of extinction angles of minerals in the thin section is one of the most common methods of petrographic microscopic practice, and at the same time one of

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* This apparatus was made in the workshop of the Geophysical Laboratory at the instigation of the writer, and can be constructed by any good mechanic.

† Compare F. E. Wright, Measurement of the Optic Axial Angle of Minerals in the Thin Section, this Journal (4), xxiv, 317–369, 1907.

the least satisfactory when accurate results are desired. It is an exceedingly easy matter to measure, with one trial only and on favorable sections, extinction angles with a probable error of ±1° to 2°, but to do so within ±1° is a very different matter. In the foregoing pages the problem is first discussed theoretically, and the mathematical equations covering the different methods applied to extinction angle measurements derived and discussed briefly. The methods for this purpose may be grouped into two classes,—those of general application and those of limited applicability. The first class may again be subdivided into two classes; either (1) the crystal is revolved between crossed nicols about its position of true extinction, or (2) the crystal remains stationary, and the accuracy of its position of true extinction tested by revolving the upper nicol or by inserting one of several different optical devices to increase the sensitiveness of the test under the prescribed conditions of illumination. These devices include the Calderon ocular, the Bertrand ocular, the Bravais-Stöber plate, the Traube plate, also twinned plates and wedges of selenite, artificially twinned plates and wedges of quartz, the circularly polarizing bi-quartz wedge plate and the bi-nicol ocular, all of which are described briefly above. Of these devices the last two are the most universal and can be so used under any given conditions of illumination that the phenomena observed are the most sensitive possible to attain by devices of this type.

On comparing the relative sensitiveness of the different methods under the same conditions, it is found that the method of testing the position of true extinction for the crystal by revolution of the upper nicol is, on colorless mineral-plates, at least twice as sensitive as that of simply turning the crystal to its position of apparent maximum darkness under crossed nicols. Under the same conditions the methods requiring the use of one of the several plates or wedges mentioned above are at least four times as sensitive as the ordinary method. With the exception of the last two devices, however, these different plates do not furnish equally sensitive results for the different conditions of illumination which may arise. In accurate work adjustable sensibility is of prime importance, particularly if a given device is to be of general application. These requirements are best filled by the bi-quartz wedge plate, by means of which the angle of rotation can be varied from 0° to any desired angle. The two halves of this wedge rotate in opposite directions, and on insertion that angle of rotation can be secured for which the contrast in the intensity of the halves of the field is most striking for a slight deviation of the crystal from its true position of extinction.

An application of the bi-quartz wedge plate, together with an artificially twinned quartz-plate or wedge, to the accurate adjustment of the petrographic microscope is considered in outline in the second part above, and a method of procedure for accomplishing the same indicated.

In part 3 a simple device for holding and rotating small crystals for the purpose of determining extinction angles or for measuring optic angles directly, is described briefly, such an apparatus having been found peculiarly useful in work with artificial crystals.

Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, D. C., June, 1908.

ART. XLI.—*The Bi-quartz Wedge Plate Applied to Polarimeters and Saccharimeters;* by FRED. EUGENE WRIGHT.*

IN the preceding paper on the measurement of the extinction angles of mineral plates in the thin section, the general theory of the relative intensity of illumination of the field for different positions of the nicols and also of the crystal section is developed. The different methods for crossing the nicols accurately and also for determining the position of total extinction for a crystal section are considered with respect to their sensitiveness, and the conclusion reached that the best results are obtained by dividing the field into parts in which the planes of polarization are inclined at equal but small angles ($90-\phi$ of the general formula) to the line of division between them (half shade system).† For given conditions of illumination and sensitiveness of the observer's eye, there is always a certain angle ($90-\phi$) for which the phenomena observed are most sensitive to slight movements from the position of true extinction. To reach the maximum efficiency of the half shade device, this angle ($90-\phi$) should therefore be adjustable within the limits prescribed by these conditions.

The conditions for maximum sensitiveness have been worked out for polarimetric purposes with sufficient care and accuracy by a number of investigators,‡ and several instruments have been designed in which high precision is possible, provided only that light of a certain quality and intensity is available and that the substance under investigation (sugar, for example) permits just the right quantity of this light to pass through it to fall within the rather narrow limits in which the observer's eye is most sensitive. In practice, these conditions have proved somewhat exacting, and considerably greater elasticity in the adjustment of the optical system of the instrument with a view to service under a greater variety of experimental conditions, without loss of accuracy, is desired. Mr. Frederick Bates§ of the Bureau of Standards has recently successfully designed an instrument in which this feature has received attention. His polariscope follows the Lippich system with the addition of sets of gear wheels for revolving the large polarizer and analyzer simultaneously in such a way that the angle of revolution of the polarizer at every instant is twice that of the analyzer. He has also demonstrated that the small angle (δ) between the

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* The author is indebted to Dr. Arthur L. Day of this laboratory for several important suggestions in the preparation of this paper.

† S. Nakamura, Centr. f. Min., 1905, p. 267-279; P. G. Nutting, Bulletin, Bureau of Standards, iii, 249, 1906.

‡ See Winkelmann, Handbuch der Physik (2), vol. vi, pp. 1362-3.

§ Bulletin of the Bureau of Standards, iv, 461, 1907.

normal to the principal plane of the analyzer and the bisector of the angle between the nicols of the Lippich polarizer can be readily compensated by a slight shift of the zero in the quartz compensator scale. This apparatus is easily superior to the ordinary quartz compensating polarimeter and is of more general application, but it is mechanically difficult and expensive to build and its adjustments are rather sensitive to wear and tear. It therefore occurred to the writer that the bi-quartz wedge plate described in the foregoing paper might serve the same purpose much more simply and therefore be of some practical utility in polarimetric and saccharimetric measurements. By means of this wedge the plane of vibration of waves from the analyzer is made to rotate from 0° to any specified angle by varying the thickness of the wedge employed, the rotation of the one half being right-handed and the other left-handed.

Since the problem of saccharimetry from the practical standpoint reduces to the determination of the exact angle of rotation of the plane of polarized light after its passage through the sugar solution, or, in brief, to the accurate setting of the analyzer or the compensating system with the analyzer, it is apparent that the bi-quartz wedge plate is directly applicable.

The mode of application is the same whether a monochromatic or a white light source is used. If monochromatic light is employed a feasible arrangement of the apparatus is shown in diagram in fig. 1. The monochromatic light, properly restricted in wave length and as intense as possible, is polarized by the nicol prism P. On passing through the solution T its plane of polarization is rotated and the angle of its rotation is determined by revolving the analyzer (fitted with an accurately divided degree circle C) until darkness ensues. The exact position of extinction is then found by inserting the bi-quartz wedge, which offers opportunity for a finer adjustment, and ascertaining that the intensity of illumination of both halves of the wedge is precisely equal for all positions of the wedge plate.*

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* The wedge plate should be mounted in a metal frame arranged to slide like the quartz compensator in accurate grooves. The quartz wedge plate used in the examination of extinction angles in crystals is 35^{mm} long, 12^{mm} wide, and is made up of wedges $0{\cdot}3^{\mathrm{mm}}$ thick at one end and $0{\cdot}5^{\mathrm{mm}}$ at the other, which are underlain by two quartz plates each $\cdot 35^{\mathrm{mm}}$ thick. The rotary angle range in each half is from $-1{\cdot}1°$ to $+3{\cdot}2°$.

For general polarimetric work, in view of the limited sensitiveness of the eye and the difficulty in obtaining homogeneous illumination of sufficient intensity, it is desirable that the angle $\frac{a}{2}$ should be capable of being increased to 15°. To accomplish this in a single wedge it would be best to make it 50^{mm} long, 10 or 12^{mm} wide with the thin end of each wedge 35^{mm} and the thick end $1{\cdot}10^{\mathrm{mm}}$ in thickness, combined with quartz plates $0{\cdot}4^{\mathrm{mm}}$ thick. This gives a pitch to the wedge of 1·5 : 100 or 8°. The point of zero deflection or the position of the black band will fall $3{\cdot}3^{\mathrm{mm}}$ from the thin end and the deflection on the thick end will be ± 15° for sodium light. The total thickness of the wedge plate is $1{\cdot}5^{\mathrm{mm}}$. Canada balsam should be used for the cementing material and care must be taken to have the wedge surfaces adjacent to the Canada balsam and also the two surfaces of the complete wedge plate parallel.

Moreover, if the wedge is inserted horizontally and at such a point that its effect on the plane of polarization of transmitted light is precisely zero, a straight, black, vertical band appears in each half of the field similar to the bands in the Babinet compensator (fig. 2). By means of this band, the true position of the analyzer can be found with great accuracy, for the setting is thus made to depend upon the exact alignment of two black bands and the photometric principle of comparing two dimly lighted fields is for the most part eliminated.

Fig. 1.

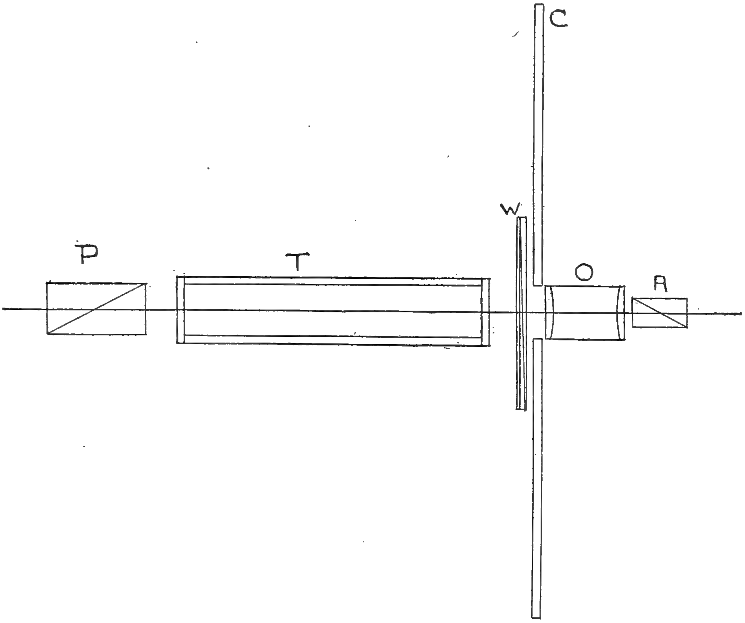

Fig. 1. Proposed arrangement of parts in polarimeter, using bi-quartz wedge plate as sensitive device. P, polarizer: T, sugar solution tube; W, bi-quartz wedge; C, degree circle of analyzer; O, Ramsden ocular; A, analyzer. Although the bi-quartz plate wedge may or may not be attached to the revolving circle mechanism, it seems preferable that its carriage should remain in one plane. The ocular O may be used either in front or back of the analyzer A, and may be a single acromatic lens in place of the positive ocular. Observations can also be made without the aid of the ocular and thus an increase of light intensity gained.

Another advantage of this system lies in the fact that the boundary lines between the halves of the wedge can be made of knife-edge sharpness without the disturbing division line in the center of the field produced by the total reflection and consequent depolarization of light waves on the edge of the small prism of the Lippich system. The edges of the two halves of the bi-quartz plate are first polished and then cemented with Canada balsam, which has practically the same refractive index (1·540 compared with 1·544), so that no appreciable total reflection with the accompanying depolarization occurs. This is the same result which was successfully attained by Brace,* who expended an extraordinary amount of care and ingenuity in an effort to free the field from this disturbing dividing line; but his instrument is not of such mechanical construction as to lend itself readily to ordinary laboratory use.

Fig. 2.

Still another favorable feature of the wedge plate scheme for adjusting the sensibility of a polarimeter is the position of the accumulator or magnifying lens of short focal length, which is necessarily of greater light intensity than the telescopic ocular usually used to view the polarizing system.

Fig. 3.

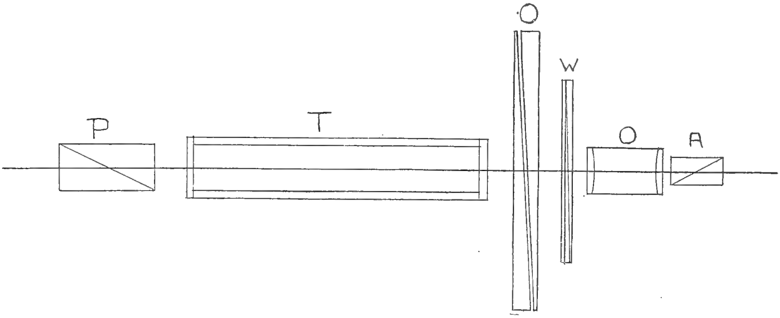

Fig. 3. Proposed arrangement of parts in quartz compensating polariscope using bi-quartz plate wedge as sensitive device. P, polarizer: T, sugar solution tube; Q, quartz compensating system; W, bi-quartz wedge plate; O, ocular; A, analyzer. As in fig. 1, the ocular O may be used either in front of or back of the analyzer; a single achromatic lens may be substituted for the Ramsden ocular, or the magnifying lenses may be done away with altogether.

If a quartz compensating system be used and a white light source, the arrangement outlined in fig. 3 might prove advantageous. The quartz compensating system has been adopted on

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* D. B. Brace, Phil. Mag. (6), v, 161, 1903.

most commercial saccharimeters in order that white light may be used, taking advantage of the fact that the rotatory dispersion of sugar solutions is approximately that of quartz. According to the scheme of fig. 3, plane polarized white light emerges from the polarizer P, passes through the sugar solution T, the different wave lengths being rotated through different angles and thence through the quartz compensating system Q, where they are again united and reduced to a common plane of vibration,—that of the original polarizer. The quartz compensating system is inserted until the field when observed through the analyzer appears totally dark. As in the preceding case, this condition is verified with the greatest sensitiveness by inserting a bi-quartz plate wedge W.

Up to this point, the advantages offered by the bi-quartz plate wedge are mainly those of simplicity, both in construction and in manipulation, and of greatly decreased cost, without any corresponding sacrifice of accuracy or sensitiveness. Its sensitiveness is adjustable within any limits likely to arise in usual polarimetric work; it is equally adaptable to the monochromatic and to the quartz compensating systems; it is possible with it to do away in considerable part with the photometric principle by the use of Landolt's bands; and finally, the line of division between the hemispheres is so narrow as to be practically invisible as an independent line.

Furthermore, in so far as it avoids the small prism of the Lippich polarizing system, it also avoids an error which is inherent in this system, and incidentally also in the Bates system, due to the loss of light in one half of the field in passing into and out of this superposed prism.* In his analysis of the problem, Bates has shown that the small angle δ between the normal to the principal plane of the analyzer and the bisector of the angle between nicols of the Lippich polarizer, can be allowed for by a slight shift of the zero of the quartz compensating scale for which provision is made in his apparatus. A slight additional correction of the same character made at the same point will also serve to correct for the loss of light by reflection at the end surfaces, and by absorption within the small prism. Supposing this to amount to 10 per cent of the total intensity, the situation can be summed up as follows: If a be the angle between the two prisms of the Lippich polarizer, I the intensity of the light from the large polarizer, then

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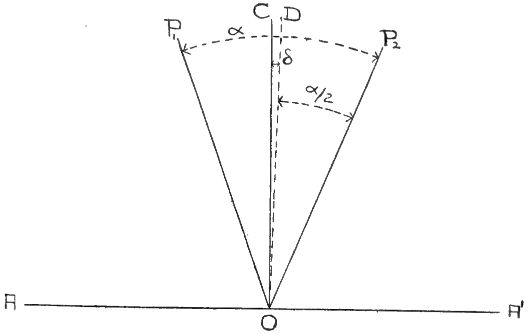
* It will be recalled that the Lippich system consists, either for monochromatic light or with the quartz compensator and white light, of a large nicol in front of which is placed a small nicol covering one-half the field of the former. The plane of polarization of this nicol makes a small angle with the plane of the large nicol. In the matter of the loss of light at the surfaces and by absorption within prisms, the system is therefore not symmetrical with respect to the line dividing the fields.

the intensity I′ of the light emerging from the small nicol will not be precisely $I' = I \cos^2 \alpha$, but $I' = \cdot 9\, I \cos^2 \alpha$.

If the two fields are matched to show equal intensity, the plane of the analyzer will not in general coincide with the bisector of the angle α, but will include with it a small angle δ (fig. 4).

FIG. 4.



An equation from which the angle δ can be figured when a is given has been derived by Bates, but his expression as noted above does not take cognizance of the loss of light in the extra prism and accordingly requires slight modification.

Let OP_1 = direction of plane of large polarizer

OP_2 = direction of plane of small polarizer

a = angle between two polarizers; angle between the normal (OC) to the plane of analyzer AA_1, and I_1 intensity of light in the field covered by the large polarizer alone when viewed through analyzer; and I_2 intensity of light of the field covered by the small polarizer. The angle P_1OA angle between large polarizer and analyzer is

$$\sphericalangle P_1OA = \frac{\pi}{2} - \frac{a}{2} + \delta$$

while

$$\sphericalangle P_2OA = \frac{\pi}{2} - \frac{a}{2} - \delta$$

From the intensity formula of the preceding article:

$$I_1 = \cos^2 \sphericalangle P_1OA = \sin^2\left(\frac{a}{2} - \delta\right)$$

$$I_2 = \cdot 9 \cos^2 a \cos^2 \sphericalangle P_2OA = \cdot 9 \cos^2 a \sin^2\left(\frac{a}{2} + \delta\right)$$

The condition of matched fields is

$$I_1 = I_2$$

or

$$\sin^2\left(\frac{a}{2}-\delta\right) = \cdot 9 \cos^2 a \sin^2\left(\frac{a}{2}+\delta\right)$$

or

$$\sin\frac{a}{2}\cos\delta - \cos\frac{a}{2}\sin\delta = \sqrt{\cdot 9}\cos a \sin\frac{a}{2}\cos\delta + \sqrt{\cdot 9}\cos a\cos\frac{a}{2}\sin\delta$$

$$\sin\frac{a}{2}\cos\delta\left(1-\sqrt{\cdot 9}\cos a\right) - \cos\frac{a}{2}\sin\delta\,(1+\sqrt{\cdot 9}\cos a) = 0$$

$$\therefore \quad tg\,\delta = \frac{1-\sqrt{9\cos a}}{1+\sqrt{\cdot 9\cos a}}\cdot tg\,\frac{a}{2}$$

or

$$tg\,\delta = \frac{1{\cdot}05409 - \cos a}{1{\cdot}05409 + \cos a}\cdot tg\,\frac{a}{2}$$

The formula of Bates expressed in this notation reads

$$tg\,\delta = \frac{1-\cos a}{1+\cos a}\cdot tg\,\frac{a}{2} = tg^3\,\frac{a}{2}$$

and differs from the above only in the constant in the fraction. For the sake of comparison the angles δ have been figured for a = 1° to 15° by both formulas and included in the following table:

$\frac{a}{2}$	δ (new formula)	δ (Bates formula)
0°	0′	0′
1°	2′	0′
2°	3′	0′
3°	4′	1′
4°	7′	1′
5°	10′	2′
6°	14′	4′
7°	18′	6′
8°	22′	10′
9°	28′	14′
10°	35′	19′
11°	43′	25′
12°	52′	33′
13°	1°03′	42′
14°	1°16′	53′
15°	1°30′	1°06′

This table as well as a discussion of the two formulae shows that the angle δ is increased in every instance by reason of the loss of light by reflection in the small nicol prism.

These differences can be allowed for upon the scale of the quartz compensator. The operation for any angle a consists in first adjusting the zero of the quartz compensator scale with respect to the analyzer without intervening sugar solution until the illumination of the two halves of the Lippich polarizer system is the same. After the introduction of the sugar solution, the quartz compensator is inserted until the original equal intensity of the halves is restored and the angle of rotation derived directly from the compensator scale.

This being the case, it would considerably simplify the construction to allow the analyzer to remain rigidly fixed and to revolve the two nicol prisms of the Lippich polarizer system, thus eliminating the complicated gearing of the Bates polariscope, which mechanically is an exceedingly difficult piece of apparatus to construct and to operate without lost motion. The revolution of the polarizing prisms in equal and opposite angles can be accomplished either by means of the worm thread device adopted in the binocle ocular of fig. 11 of the preceding article, or by a grooved arm into which pins connected with the supporting collars of the nicols fit and slide as the arm is inserted. Mechanically these devices are not difficult of construction and the angle of revolution can be read off accurately.

In the foregoing pages the bi-quartz plate wedge is suggested as a simple and effective basis for the construction of a polarimeter of adjustable sensibility in which the error from the asymmetry of the Lippich system, together with all the serious complications of mechanism, are completely avoided without loss of accuracy. Such a plate has been constructed and successfully applied to the exact location of crystal extinctions, but unfortunately pressure of other duties has prevented the writer from actually constructing a saccharimeter. Through the courtesy of Dr. Bates of the Bureau of Standards, however, an opportunity was given to test the wedge on a large and accurate standard polarimeter illuminated by homogeneous green light from a mercury quartz-glass arc. Its performance was entirely satisfactory, minute displacements of the analyzer from its position of true extinction being readily detected.

Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, D. C., July 6, 1908.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *Determination of Phosphorus in Phosphor Tin.*—Gemmel and Archbutt have devised a new method for making this somewhat troublesome determination. They place two to five grams of the sample in a 500^{cc} Jena flask fitted with a tap funnel and delivery tube. The tap funnel has a two-way stop-cock, allowing gas or liquid to be introduced as desired. The absorption apparatus consists of three Drechsel bottles, the first two charged with bromine and water, the last with bromine water only. The air is first removed by passing carbon dioxide, then 50 to 100^{cc} of concentrated hydrochloric acid are introduced, and the contents of the flask gently heated and finally boiled until the substance is dissolved. Finally a current of carbon dioxide is again passed through the apparatus in order to drive forward any remaining traces of hydrogen phosphide, the liquids in the absorption apparatus are transferred to a beaker, evaporated to small volume, and the phosphoric acid is precipitated with magnesium mixture in the usual manner. It is to be observed that any arsenic present in the substance would pass over with the phosphorus, but the authors did not find this element present in the samples that they examined. It was found that the actual evolution and absorption occupies less than twenty minutes, so that the process is shorter and simpler than those usually employed. Upon comparison with the methods consisting in the fusion, with "hepar sulphuris" and with potassium cyanide, of the products of treatment with nitric acid the new method was found to give much more concordant results.—*Jour. Soc. Chem. Indus.*, 1908, 427. H. L. W.

2. *Complex Calcium Salts.*—By the action of cæsium sulphate solution upon gypsum, D'Ans has prepared a very stable double sulphate $Cs_2Ca_2(SO_4)_3$. The calcium alkali double sulphates now known, of which the first is the mineral syngenite, are as follows:

$K_2Ca(SO_4)_2.H_2O$	———	$K_2Ca_5(SO_4)_6.H_2O$
$(NH_4)_2Ca(SO_4)_2.H_2O$	$(NH_4)_2Ca_2(SO_4)_3$	$(NH_4)_2Ca_5(SO_4)_6.H_2O$
$Rb_2Ca(SO_4)_2.H_2O$	$Rb_2Ca_2(SO_4)_3$	———
———	$CO_2Ca_2(SO_4)_3$	———

D'Ans has prepared also two interesting triple salts analogous to polyhalite, $Ca_2MgK_2(SO_4)_4.2H_2O$. These are the salts $Ca_2Cu(NH_4)_2(SO_4)_4.2H_2O$ and $Ca_2CdK_2(SO_4)_4.2H_2O$, which were prepared by boiling solutions of the proper salts with gypsum. It is probable that a considerable number of compounds analogous to polyhalite and to krugite, $Ca_4MgK_2(SO_4)_6.2H_2O$, may be prepared, and it is the author's intention to continue his investigations in this direction.—*Berichte*, xli, 1776. H. L. W.

3. *Radio-activity.*—MARCKWALD has recently delivered a lecture before the German Chemical Society giving a good account of what has been done in the field of radio-activity, and discussing the prevailing views in regard to this subject. While this lecture contains little that is new to those who are familiar with the literature of the subject, it will be useful to those who desire a general knowledge of this new branch of science. The author gives a somewhat novel view of the enormous energy involved in the transformation of the radio-active elements by saying: "It was the dream of the alchemists to transmute base metals into noble ones. The radio-active substances teach us that, if this process could be achieved, there would either be obtained at the same time so much energy that in comparison to it the value of the noble metal would be insignificant, or on the other hand the consumption of energy would render the ennobling of the metal practically uneconomical."—*Berichte*, xli, 1524. H. L. W.

4. *A Simple Method for Determining Vapor Densities.*—BLACKMAN has devised an apparatus for this determination, which consists of a sealed tube in which is placed a capillary tube graduated in millimeters, closed at one end, and supplied with a thread of mercury at the other end in order that it may serve as a manometer. It is evident that when this system is heated with nothing but air within and without the manometer the pressures will continually balance each other; but in the operation of determining a vapor density a weighed amount of volatile substance is placed in the sealed tube with the manometer, and when this substance is volatilized by heating it exerts a pressure which can be measured by the movement of the thread of mercury in the capillary manometer. Then, when the two temperatures and the volume of the apparatus are known, the vapor density of the substance can be calculated from the pressure produced by it. The calculations are somewhat complicated, and the execution of the operation does not appear to be as simple with this apparatus as with that of Victor Meyer; but the method is interesting in its novelty.—*Zeitschr. physikal. Chem.*, lxiii, 48. H. L. W.

II. GEOLOGY.

1. *La Montagne Pelée après ses Eruptions;* par A. LACROIX. 4°, pp. 136, figs. 321, Paris, 1908 (pub. by the Academy of Sciences).—This is a supplement to the author's great work *La Montagne Pelée et ses Eruptions*, published a few years ago and noticed in this Journal (vol. xix, 465). From a variety of sources the writer has collected a considerable body of facts, which interpreted by the light of his former investigations, he uses to describe the progressive changes which have occurred in the diminishing volcanic activity, and in topography, owing to erosion and the crumbling of the dome of lava. Very interesting are the views showing the rapid growth of vegetation everywhere

over the destroyed area, which now largely conceals the traces of the great catastrophe. Already the streets of Saint-Pierre are being cleared out and are beginning to be rebuilt by the new population settling there.

The writer discusses the structure of the dome of Pelée and, after comparison of the texture of its rocks with those of American laccoliths, is led to the conclusion that the effect of pressure in determining the micro-granular texture of quartzose igneous rocks is much less than has been generally supposed.

In the third chapter different types of volcanic eruption are considered; the author makes four classes: *a*, the Hawaiian, in which the lavas are extremely fluid and the vapors escape without causing projection of solid material; *b*, the Strombolian, in which the lava is more viscous and the escape of vapors takes place with explosive activity with the projection of some pasty material which falls as rounded, flattened bombs; *c*, the Vulcanoan, in which the lava solidifies at the surface between eruptions, and this, and the very viscous condition it is in, causes the explosions and escape of the gases to be accompanied by quantities of broken solidified rock, which falls as angular bombs, lapilli, etc.; *d*, the Peléean, whose explosion occurs in material already solidified, giving rise to incandescent clouds composed of an intimate mixture of gas and solid material whose weight is so great that they roll rapidly down the mountain side, if not contained more or less in a caldera of sufficient size, producing the direful effects seen at Saint Pierre. It will be noticed that this classification is a progressive one depending on the proportions of gas and solid material and on the relative condition, liquid or solid, of the magma. It could be reduced to two, the Strombolian, of which the Hawaiian is an extreme case in one direction, and the Vulcanoan, of which the Peléean is an extreme case in the other. These definitions, which are essentially those employed by the Italian geologists, are more precise than the "quiet" and "eruptive" types of the geological text-books.

The author calls attention to the fact that many volcanoes vary between these types according to the character of their magma, but that such variation may take place in the history of a single volcano and even in a single eruption.

In the final portion of the work the writer discusses various phenomena occurring at Vesuvius in relation to those at Monte Pelée. He describes the avalanches of dry volcanic dust and ashes caused by the accumulations on the steep sides of the cone. These leave ravines behind them which become accentuated by rain wash and this produces the curious umbrella-like relief of the mountain.

In conclusion a study of the facts obtainable of the eruption of '79, which destroyed Pompeii, leads the author to the view that this phenomenon was of the regular Vesuvian type, and that the destruction, occurring through a period of several days, was caused by the excessive fall of cold, or at least only warm, ashes and lapilli, aided by earthquake shocks. On the other hand, the occurrence at Saint Pierre, occasioned by the sudden descent of an incandescent cloud, is to be regarded as unique in the history of catastrophes caused by volcanic eruptions. L. V. P.

2. *Publications of the United States Geological Survey.*—Recent publications of the U. S. Geological Survey are noted in the following list (continued from p. 97 of this volume):

TOPOGRAPHIC ATLAS.—Twenty-seven sheets.

FOLIOS—No. 157. Passaic Folio, New Jersey–New York. Description of the Passaic Quadrangle; by N. H. DARTON, W. S. BAYLEY, R. D. SALISBURY, and H. B. KÜMMEL. Pp. 27, with 4 maps.

No. 159. Independence Folio, Kansas. Description of the Independence Quadrangle; by F. C. SCHRADER. Pp. 7, with Table of Formation Names, 3 maps, and Columnar Sections.

MONOGRAPH. Vol. xlix. The Ceratopsia; by JOHN B. HATCHER. Based on preliminary studies by OTHNIEL C. MARSH. Edited and completed by RICHARD S. LULL. Pp. 198, with xlix plates, 125 figures. This volume was noticed on page 98 of this volume.

Professional Paper 62. The Geology and Ore Deposits of the Cœur D'Alene District, Idaho; by FREDERICK LESLIE RANSOME and FRANK CATHCART CALKINS. Pp. 203, with xxix plates, 23 figures.

BULLETINS.—No. 335. Geology and Mineral Resources of the Controller Bay Region, Alaska; by G. C. MARTIN. Pp. 141, with x plates, 2 figures.

No. 337. The Fairbanks and Rampart Quadrangles, Yukon-Tanana Region, Alaska; by L. M. PRINDLE. With a section on the Rampart Placers, by F. L. HESS: and a Paper on the Water Supply of the Fairbanks Region, by C. C. Covert. Pp. 102, v plates, 3 figures.

No. 340. Contributions to Economic Geology, 1907. Part I.—Metals and Non-metals, except Fuels; C. W. HAYES and WALDEMAR LINDGREN, Geologists in charge. Pp. 482, with vi plates and 26 figures.

No. 344. The Strength of Concrete Beams. Results of Tests of 108 Beams (First Series) made at the Structural-material Testing Laboratories; by RICHARD L. HUMPHREY. Pp. 58, with I plate and 13 figures.

No. 345. Mineral Resources of Alaska. Report on Progress of Investigations in 1907; by ALFRED H. BROOKS and others. Pp. 294, with v plates, 7 figures.

No. 346. Structure of the Berea Oil Sand in the Flushing Quadrangle, Harrison, Belmont, and Guernsey Counties, Ohio; by W. T. GRISWOLD. Pp. 28, with II plates.

3. *Graptolites of New York, part 2, Graptolites of the Higher Beds*, by R. RUEDEMANN, Mem. 11, N. Y. State Mus., 1908, pp., 583, plates 31.—In this volume, indispensable both for students of graptolites and of stratigraphy, Doctor Ruedemann completes

his studies of the New York graptolites above the lower third of the Ordovician. Part 1 was published in 1905. The last of the graptolites are found in the middle Devonian (Hamilton). He discusses 109 Ordovician, 25 Silurian and 11 Devonian forms.

An interesting table shows the range of the graptolite genera of the United States; this brings out the fact that Dictyonema ranges through all strata in which graptolites occur, but as a rule the genera are short-lived. There are three important outbursts of generic development: (1) the dichograptid type of the lower Ordovician, (2) the dicellograptid-diplograptid of the middle Ordovician, and (3) the monograptid of the Silurian. C. S.

4. *Fourth Report of the Director of the Science Division, etc.* N. Y. State Museum, Bull. 121, 1908, pp. 203, with many plates.—The annual statement of progress in the various science divisions of the New York State Museum is here presented in interesting form by the Director, Dr. J. M. Clarke. A description is given of the new museum planned, as far as the ground plan is concerned; the available space will be 80,000 square feet and the exhibition rooms will be lighted from the top. The first American Helianthaster is described as *H. gyalum.* The closing paper by the Director on "The beginnings of Dependent Life" describes the "material from the faunas which might illuminate the incipient expressions of dependent life. It is through this avenue only that the problem of the origin of the symbiotic conditions which now pervade all nature can ultimately be approached with hope of resolution." C. S.

5. *Rocks and Rock Minerals. A Manual of the Elements of Petrology without the Use of the Microscope;* by LOUIS V. PIRSSON. Pp. v, 414. New York, 1908 (John Wiley & Sons).—Recent progress in the knowledge of rocks has so largely resulted from the development of the various methods of study employing the microscope that modern text-books of petrology have naturally been chiefly devoted to them. It still remains true, however, that from many points of view, scientific as well as practical, rocks must be studied by other than microscopic methods, and it is to this important side of the science that the present volume is devoted; its appearance will be welcomed alike by teachers, field geologists, and technical men. Such a volume has long been needed, and the author's experience both in teaching and in active investigation has peculiarly fitted him for its preparation. The work as a whole, after two opening chapters of general character, is divided into two parts: the first (pp. 21–131) deals with rock-making minerals, their characters and the methods for their determination; the second (pp. 132–408) discusses the various types of rocks, igneous, stratified, and metamorphic, closing with a chapter on their determination. The style is throughout clear and interesting, and abundant illustrations, largely from original sources, have been introduced; the half-tone engravings especially deserve commendation for their admirable execution, due to the fact that they have been printed, not with the text, as is too often the case, but as separate plates.

III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *The Shaler Memorial Expedition to Brazil and Patagonia, 1908–09,* J. B. WOODWORTH in charge. [From a letter to the Editors, dated Curityba, Paraná, Brazil, August 6, 1908.]—The members of the Shaler Memorial Expedition to Brazil reached Rio de Janeiro on the 8th of July. Since that time they have journeyed southwards through the states of São Paulo and Paraná under the guidance of Dr. Derby, Director of the Geological Survey of Brazil, in a reconnaisance of the conglomerate formations of the Permo-Carboniferous, with a view to selecting areas for a more detailed study of the supposed glacial deposits of that terrane. On entering the state of Paraná, in a railway cut between Itararé and the Rio Jaquaricatee, the writer was shown two bowlder beds in which well striated and scrubbed pebbles and stones were at once discovered; fragmental materials in all respects like those in the Pleistocene till beds of the glaciated area of North America and of the Permo-Carboniferous beds of South Africa and Australia. The work, in conjunction with Dr. Eusebio P. de Oliveiro, Assistant Geologist of the Geological Survey of Brazil, will now be directed in part along the border of these deposits and the Devonian and Pre-Devonian crystalline terranes, to the finding, if possible, of a glaciated floor such as that already known in India, South Africa and Australia.

J. B. WOODWORTH.

2. *British Association for the Advancement of Science.*—The seventy-eighth annual meeting of the British Association, held at Dublin during the week beginning with Sept. 2, was remarkable for its size, 2270 members being in attendance. It was also notable for the interest aroused by several of the addresses, as particularly that of the President, Dr. Francis Darwin, (Nature, Sept. 3) on the movements of plants, and that of Prof. John Joly on radium and its parent uranium as the source of the earth's internal heat (ibid., Sept. 10). It is announced that the meeting of the Association in 1909 is to be held at Winnipeg from Aug. 25 to Sept. 1; that of 1910 at Sheffield and of 1911 at Portsmouth.

OBITUARY.

M. ANTOINE HENRI BECQUEREL, the eminent French physicist, whose discovery of the so-called "Becquerel rays" prepared the way for the important subject of radio-activity, died on August 25 at the age of fifty-six years.

M. E. E. N. MASCART, a second eminent French physicist, whose work lay chiefly in the departments of optics, electricity and magnetism, died on August 26 at the age of seventy-one years.

ARTHUR LISTER, of Leytonstone, England, well known for his work on the Mycetozoa, died on July 19 at the age of seventy-eight years.

PROF. ALEXIS HANSKY, of the Pulkowa Observatory, was drowned at Simeise in the Black Sea on August 11; although but thirty-six years old, he had already made important contributions to Solar Physics.

J. F. NERY DELGADO, President of the Geological Commission of Portugal, died on August 3 in his seventy-fourth year.

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The first consignment of these rare specimens was sold on sight. We have now received a second consignment of all there are, as the mine is now filled with water. They come from Wanshanchang (Hamlet of Ten Thousand Hills), Tungyen Prefecture, Prov. of Kweichow, China. They occur in ordinary and interpenetrating twins of bright ruby red color. In size the crystals are from ¼ to ¾ inches. The matrix is a pure white quartz, the crystals always occurring in cavities, with quartz crystals; prices run from $10, $15, $20, $35, $50, $75, $100, $125 and $150.

BEAUTIFUL ZEOLITES FROM THE NEW ERIE TUNNEL CUT AT BERGEN HILL, NEW JERSEY.

In making the new Erie Rd. cut through Bergen Hill, some very remarkable and beautiful specimens of zeolites were found, and I had the good luck to secure the cream of those found. We advise those who can to call personally and see these interesting and beautiful specimens. They consist of calcite in combinations with brilliant apophyllite, analcite, datolite, pyrite, and prehnite, with small mica crystals.

RARE MINERALS AND NEW FINDS.

Benitoite and Neptunite from San Benito Co., Calif.; Californite, Tulare Co., Cal.; Pink Beryl, Mesa Grande, Cal.; Diamond in matrix, New Vaal River Mine, S. Africa; Herderite, Auburn, Me.; Josephinite, Oregon; Smithsonite, Kelley, N.M.; Tetrahedrite, Cobalt, Ont. and Bingham, Utah; Vanadinite, Kelley, N. M.; Vivianite, large crystals, Leadville, Col.; Wulfenite, Organ Mts., N. M.; Native Bismuth, Cobalt, Ont.; Atacamite, South Australia; Niccolite, crystallized, Saxony, Ger.; Embolite, Broken Hill, Aus.; Argentite xls, Freiberg, Sax.; Pyrargyrite xls, Hartz; Crocoite, Siberia and Tasmania; Jade, China; Opals, Barcoo River, brown matrix; Titanite, Tilly Foster and Switz. Sphene, Switz.; Gold, in matrix, Verespatak, Siebenburgen and Nova Scotia; Algadomite, Mohawkite, Domeykite var. stibio-domeykite, all from Keweenaw Co., Michigan; Tourmaline, in feldspar and quartz, also loose crystals, from Mesa Grande, Cal., all colors.

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[FOURTH SERIES.]

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ART. XLII.—*Some New Measurements with the Gas Thermometer*; by ARTHUR L. DAY and J. K. CLEMENT.

FIRST PAPER.

MANY of the serious problems of rock formation are dependent upon the exact measurement of temperatures, in the region lying between 400° and 1600° C. It is, therefore, not surprising that a considerable portion of the energy of investigators in this branch of geophysics (see in particular Barus, Bulletins of the U. S. Geological Survey, No. 54) has had to be expended upon the methods and mechanism of high temperature measurement. This situation not only still exists, but the increasing perfection in other lines of geophysical analysis has created a demand for considerably higher accuracy in the temperature determinations, if such shall prove attainable. This has been the chief incentive for the present long, difficult and still incomplete investigation of the gas thermometer.

A discussion of gas thermometry in its more general aspects is not contemplated in the present article. This has been done from time to time by others,* and its underlying assumptions found to be sound and adequate. There is, therefore, no need to go over this ground again. On the other hand, there is no denying the fact that a great deal still remains to be done upon the experimental side before the steadily advancing requirements of both science and industry in the matter of a trust-

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* See in particular the several papers of Chappuis, published in the Travaux et Mémoires du Bureau International des Poids et Mesures and the Rapports présentés aux Congrès International de Physique; Carl Barus, Les Progrès de la Pyrométrie, Rapports présentés aux Congrès International de Physique, vol. i, page 148; E. Buckingham, Bulletins of the Bureau of Standards, vol. iii, p. 237.

worthy temperature scale of sufficient accuracy and range can be satisfied.

It is no disparagement of the present system of temperature definition to say that the gas thermometer itself is a complicated and cumbersome instrument to use in any of the forms which have hitherto been devised, and possesses limitations, both of range and of accuracy, which are very difficult to overcome. One consequence of this, particularly in the region of high temperature measurements, where errors of considerable magnitude still exist in the fundamental scale, is that temperature measurements easily come to receive a somewhat fictitious value in the hands of those who have never acquired a firsthand knowledge of these limiting conditions. This has been further facilitated by the comparative ease with which relative measurements of temperature can be made, even in the more inaccessible parts of the scale, with the thermoelement and the resistance thermometer. These devices are sensitive to temperature differences of the order of magnitude of ·01° throughout their entire range, and yet depend absolutely upon fundamental measurements with the gas thermometer for their evaluation in terms of the generally accepted degree centigrade. It is sufficiently obvious, though often carelessly overlooked, that no method of temperature measurement, however sensitive or adaptable it may be, can yield temperatures of greater absolute accuracy than the system in terms of which those temperatures are defined. With the gas thermometer as our basis of definition, therefore, we shall know our temperatures with just the certainty which it is able to furnish and no more. There is, to be sure, some justification for expressing the results of thermoelectric or resistance measurements in units smaller than the errors of the fundamental scale, provided they are so recorded that they can be translated in terms of some more accurate fundamental system when future investigations shall have provided one, or where only comparative measurement is involved; but this is also frequently overlooked.

The fundamental temperature scale now used is the centigrade scale of the Bureau International des Poids et Mesures, determined with the constant volume hydrogen thermometer from an initial pressure of 1^m of mercury. Its interpolation between the melting point of pure ice and the boiling point of pure water (0°–100°) is probably accurate to the nearest ·005°*; the extrapolation from 100°–300° may be in

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[*] The fundamental subdivision of the interval between the melting point of ice and the boiling point of water by means of the expansion of hydrogen was undertaken with great care by the Bureau International des Poids et Mesures (P. Chappuis, Trav. et Mem. d. Bur. Int., vol. vi) and is a work of such extraordinarily painstaking character in most particulars that no investigator has found it necessary to repeat it. It is commonly accorded an

error as much as ·05°. The Reichsanstalt gas thermometer scale, which is now very generally used as the basis of high temperature measurements, is officially stated to have a probable error of 2° or 3° between 300° and 1150°, and of 10° between 1150° and 1600.°

The gas thermometer problem is one in which theory is often inclined to lose patience with practice. It has been demonstrated over and over again, for example (Barus, Buckingham, loc. cit.), that the constant-pressure system of measurement ought to be more direct and free from error than the constant-volume system, notwithstanding which the major portion of the results which go to make up the real progress of the past fifty years has been obtained through the use of the constant volume principle. Theory has also been very apprehensive from time to time of the ultimate outcome of attempting to define temperature in terms of the expansion of a diatomic gas, and yet nitrogen is the only gas which has yet been found practicable for long ranges extending to the higher temperatures. It does not react with a platinum bulb and does not diffuse through its wall, and so far (up to 1600°) it has not been found to dissociate. From the laboratory side of gas thermometry, the main difficulty is now, as it has always been, to find a practicable bulb which will hold some expanding gas without loss or change through a long range of temperatures and permit sufficiently accurate measurements of the pressure-volume relation within. After more than three-quarters of a century of the most varied experiences, pure nitrogen in a platin-iridium bulb in which the pressure at constant volume can be measured, is the only arrangement which has not yet encountered some very serious obstacle to the extension of its range or its accuracy. It was therefore adopted without hesitation for the study here described.

accuracy of about ·001°, but this is probably too high on account of the uncertainty in the determination of the expansion coefficient of the thermometer bulb. This bulb was of platin-iridium (90 Pt, 10 Ir) of 1 liter capacity, and the determination of its expansion coefficient had been made by Deville and Mascart, but this determination was rejected in favor of Benoit's value, which was obtained with a different platin-iridium bar. The difference between the two determinations amounts to ·007 per cent at 50°, a quantity sufficient to affect the temperature scale at that point by about ·004°. The measurements of the same alloy which were made for the present paper (page 440) differ from Benoit's by an amount equivalent to ·002° at 50°. There are also differences between the results obtained by Benoit himself for different bars which exceed ·003° when interpreted in terms of the temperature. It is perhaps significant that these alloys were prepared before the work of Mylius on the exact determination of the platinum metals had been done. The difference may therefore point to considerable variations of composition in the alloys employed. At any rate, the uncertainty here is out of all proportion to the accuracy of the remainder of Chappuis's work (see also P. Chappuis, Rapports présentés au Congrès International de Physique, vol. i, p. 137, 1900, footnote 1).

If this somewhat circumstantially selected system does not at the moment appear to confront any insuperable obstacle, many and insidious difficulties have been encountered in the course of its development. One has only to examine the determinations of the same temperature made by different observers, all using substantially this method, to become convinced that some serious work still requires to be done to clear up the present uncertainty. The melting point of gold is given by Barus (1892) at 1092°; by Holborn and Wien (1895), 1072°; Holborn and Day (1900), 1063·5°; by Jacquerod and Perrot (1905), 1067·2°; by Day and Clement (preliminary, 1907), 1059·1°. For the moment it is sufficient merely to call attention to these differences in the results which have been obtained, and to reserve detailed comment upon them for a subsequent part of the paper. Suffice it to say that both Holborn and Day at the close of their work (1900) entertained the positive opinion that the discrepancies had occurred in the experimental details and were not chargeable to an oversight in any of the more fundamental relations involved.

With this prevailing idea in mind—that the general relations are already satisfactorily worked out and that the problem remaining is therefore primarily an experimental investigation, (1) to increase the absolute accuracy of the measurements, and (2) to extend their range—Prof. Holborn at the Reichsanstalt and the authors at the Geophysical Laboratory took up the gas thermometer again in 1904. The details were for the most part independently planned and the work has been independently carried out. In a research which offers so many technical difficulties, two independent plants were obviously better than one. In so far as a division of labor was attempted, Prof. Holborn entered at once upon the more daring undertaking, namely, to increase the range of measurement. He built a bulb of pure iridium in the hope that it might prove possible to make continuous gas thermometer measurements as far as the melting point of platinum. For this work the errors of observation were allowed to remain large, larger in fact than they had been in the joint work of Holborn and Day in 1900. The undertaking was entirely successful and yielded very satisfactory measurements up to about 1600°,* the error for the new portion of the gas scale (from 1150° on) being about 10°.

Our work was for the moment restricted to 1200° in an effort to eliminate or materially to diminish the errors which

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* Temperaturmessungen bis 1600° mit dem Stickstoffthermometer u. mit dem Spektralphotometer, Sitzungsber. Berl. Akad. xliv, p. 811, 1906; Ein Vergleichung der Optischen Temperaturscala mit dem Stickstoffthermometer bis 1600°, Ann. d. Phys. (4), xxii, p. 1, 1907.

have been inherent in all gas thermometer measurements up to this time. Progress is necessarily slow in work of this character, but we were chiefly delayed by having to build the entire equipment *ab initio*, except the bulb.*

The instrument which we constructed for this work has now been in operation for more than three years, but has never been described in print. It is of the constant volume type, as has been explained, similar in general plan to that at the Reichsanstalt, but differing from it in certain important details with the especial purpose of correcting some of the known errors of the Reichsanstalt instrument: (1) A uniform temperature along the thermometer bulb appeared to us imperative, and a much greater effort was made to obtain it; (2) the entire furnace was enclosed in a gas-tight bomb in order that a nitrogen atmosphere might be maintained with equal pressures, both inside and outside of the bulb. This had the effect of obviating any tendency of the gas to diffuse into or out of the bulb, and allowed no opportunity for the deformation of the bulb through differences between the pressure within and without. A further effect of this arrangement was to increase the sensitiveness of the instrument fully threefold. It has been the practice heretofore in such temperature measurements to greatly reduce the initial pressure of the gas in order that its final pressure at the highest temperature to be measured may be substantially equal to the atmospheric pressure without, in order that the strain on the bulb through pressure difference may be least when its power to withstand such strain is smallest. In the Reichsanstalt instrument, this restricts the available range of pressure for a temperature range from 0°–1150° to about 500^{mm} of mercury, or less than $0{\cdot}3^{mm}$ per degree. By arranging to increase the pressure outside the bulb as the pressure within increases, this restriction falls away and it is possible to extend the pressure range over the whole length of the scale which the manometer carries. The scale of our instrument was 1·8 meters long. For a range of 1200°, therefore, we were able to work with a sensitiveness of a little more than 1^{mm} for each degree centigrade, or rather more than three times the sensitiveness used in the

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*The bulb which was used for all the measurements here recorded was one of two bulbs made by Dr. Heræus, of Hanau, Germany, for the Holborn and Day investigation at the Reichsanstalt, one of which contained 20 per cent iridium and the other 10 per cent. The 20 per cent iridium bulb is still at the Reichsanstalt and was used in the publications of Prof. Holborn to which reference has been made. The 10 per cent iridium bulb was exhibited by Dr. Heræus at Paris, after which it was loaned to us for this investigation. The form and capacity of the two bulbs were substantially the same, about 200^{cc}.

The authors take this opportunity to express their thanks to Dr. Heræus for his most cordial and effective coöperation throughout this undertaking, and for his personal interest in the outcome of it.

Reichsanstalt instrument, and also to vary the initial pressure considerably without serious loss of sensitiveness. (3) In the capillary connecting link between the bulb and the manometer, we were able to diminish the volume of the unheated space to about one-third of its former value, and thereby still further to reduce one of the classical errors of gas thermometry. This "unheated space,"* it will be remembered, serves to connect the bulb which contains the expanding gas at a certain temperature and pressure, with the manometer in which the pressure is measured. This space is therefore filled with gas which forms a part of the total gas content of the bulb, but is not heated with it and therefore requires a correction the magnitude of which has sometimes been so great as to create misgivings about the trustworthiness of the resulting pressure obtained.† The ratio of the volume of the unheated space to the total volume of the bulb $\left(\frac{v}{V}\right)$ in the final form of the gas thermometer used by Holborn and Day amounted to ·0046; in the more recent instrument used by Jaquerod and Perrot, to ·0180; while in our instrument it was reduced to ·0015. The entire correction for the unheated space in our instrument therefore amounted to less than 5° at 1100° compared with about 20° in the older Reichsanstalt instrument and about 80° in the instrument used by Jaquerod and Perrot. An error of 10 per cent in the determination of the average temperature of the unheated space in our instrument will not therefore affect the result more than ·5° at this temperature. (4) The expansion of the bulb itself was redetermined with much greater care than before.

All these are details the importance of which we have come to estimate very highly, if a really accurate temperature scale based upon the expansion of a gas is to be established. The effect of a serious error in any one of the four particulars noted upon the temperature measurement is several times greater than that arising from differences in the expansion of the various available gases which formed the basis of the elaborate study by Jaquerod and Perrot to which reference has just been made. And here, perhaps, lies the kernel of the whole matter so far as it concerns the establishment of accurate fundamental temperatures in a region as remote as 1000° from the fundamental fixed points. The interest of observers is easily diverted to questions of general and theoretical interest, like the validity of the Gay-Lussac law over great temperature ranges, while experimental conditions which permit errors of considerable

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* "Espèce nuisible," "Schädlicher Raum."

† See in particular Jaquerod and Perrot, Arch. d. sci. phys. et. nat., Genève (4), xx., pp. 28, 128, 454, 506, 1905.

magnitude in an absolute scale attract altogether inadequate attention. This is obviously no aspersion upon the beautiful work of Jaquerod and Perrot, or of any other investigator, but it may be the explanation of the uncertainty in existing high temperature measurements. Jaquerod and Perrot, for example, measured the melting point of gold with the gas thermometer, using five different gases successively in the same (fused silica) bulb, with a maximum variation of only ·4°, and yet in its absolute value the determination may easily be 5° or more in error. In fact, in one of their determinations in which a porcelain bulb was substituted for silica, a difference of 4° appeared. The observation was dropped, but it serves to direct attention sharply to a possible uncertainty of several degrees arising from the corrections for the distribution of temperature along the bulb and the unheated space, and for the expansion coefficient of the bulb itself.

Somewhat more in detail, the apparatus may be described as follows:

The Furnace.—The furnace consists of a wrought iron tube of about 25^{cm} inside diameter, carrying a cast iron pipe flange at each end. To these flanges cast iron covers were fitted by grinding to a gas-tight joint. In position this bomb is vertical, and the lower cover is permanently secured in place with bolts. The furnace tube is made from a magnesite mixture* about 36^{cm} long and 6^{cm} inside diameter within which the furnace coil is wound. This scheme of winding the heating coil on the inside of a refractory tube is very successful in its operation and is not difficult. With a pure platinum coil (melting point about 1750°) a furnace temperature of 1600° can be reached without danger to the coil and maintained for some time if desired. There is considerable loss of platinum through sublimation in maintaining a resistance furnace at this temperature, so that it is necessary to use a wire of considerable size if it is required to maintain so high a temperature for long periods of time. The gain over the same coil wound on the outside of a thin porcelain tube is about 200° (1600° instead of 1400°) for the same current and conditions of insulation. The method of winding is simple. A series of five wooden wedges is grouped together so as to collapse when the center one is removed. When grouped and fastened together the outside surface is turned down to a cylinder of exactly the size which the finished coil is to have. This multiple wedge then serves as a collapsible arbor and the coil is wound upon it with any desired arrangement of turns. A piece of paper or thin cardboard between the wire and the arbor sometimes facilitates the removal of the arbor after completion. The arbor with the

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* Harbison-Walker Refractories Company, Pittsburg, Pennsylvania.

coil upon it is then placed in position in the cylinder and the remaining space between it and the cylinder wall filled with magnesite cement of the same composition as the tube itself. When this has set the arbor can be removed, leaving the coil in position in the tube. It then remains merely to go over the exposed wire with a very thin coating of the same cement and the coil is ready for use. Such a coil is less liable to displacement through expansion and contraction than when the winding is on the outside of the tube. We have had such coils in constant use for a variety of purposes in the laboratory for several years, and have found them durable, economical and most convenient.

In this particular furnace the windings are somewhat closer at the top and bottom of the coil than at the middle, in order to provide a more uniform temperature from one end to the other. This scheme, although efficient and perfectly satisfactory for most purposes, will not provide a perfectly uniform distribution of temperature over long temperature ranges. An arrangement of the turns which is adequate for low temperatures will not provide sufficient compensation at the ends for much higher ones. We therefore prepared two secondary coils of finer platinum wire in which the current could be independently varied, and mounted them within the main coil at the two ends of the tube. These coils extended into the tube about 7^{cm} from each end and were fastened in position by smearing with the magnesite cement as before. With this arrangement, we are able to obtain a temperature distribution along the bulb which did not vary more than 1° for all temperatures up to 1200°. We have not yet attempted to go beyond this point. To ascertain exactly what the temperature distribution was at the moment of any pressure measurement, it was necessary to use three thermoelements simultaneously, one principal element at the middle of the bulb and secondary elements at each end. These elements were carried out of the furnace between two discs of rubber packing in the center of the cover.

The bulb was symmetrically located in the center of this furnace, the capillary stem extending out of the top of the heating tube and then with a gentle bend of 90° passing out of the metal bomb at the side of the cover, as can be seen in the diagram (fig. 1). It was then connected by means of a second smaller capillary of platinum with the top of the manometer tube near the point of constant level adjustment. The iron bomb thus prepared was water-jacketed around the sides and at the top and bottom, which effectually prevented any of the furnace heat from reaching the manometer which stood beside it. The scale and mercury columns of the manometer therefore suffered no exposure to temperature variation other than that which existed in the room, and the latter, if serious, as it sometimes was in the summer months, yielded to the increased air circulation produced by an electric fan.

When the furnace was mounted in position, the cover, from which hung the thermoelements and the bulb, was permanently

Fig. 1.

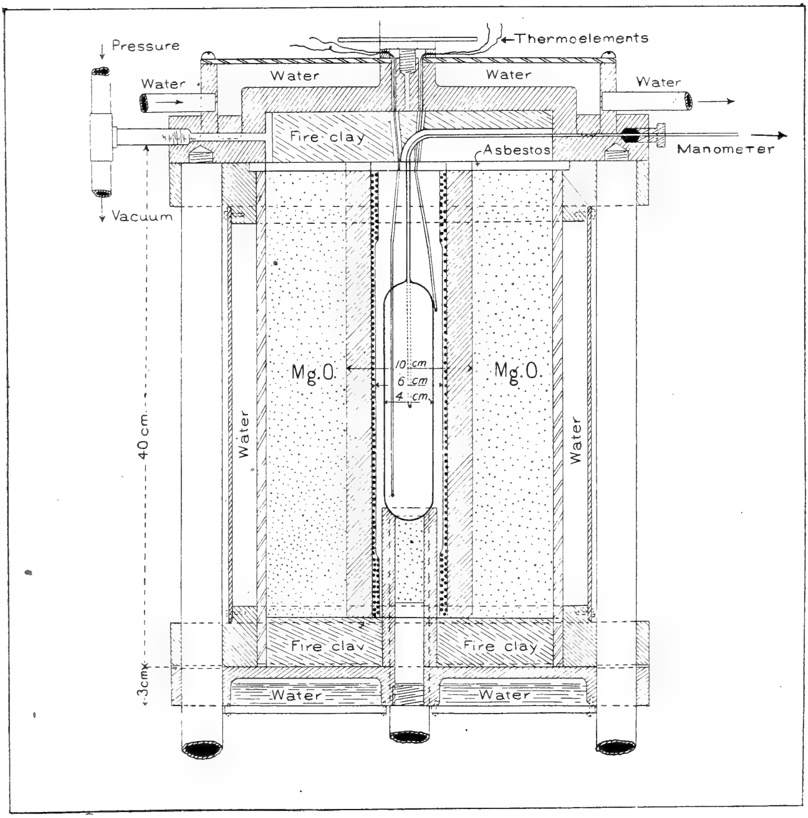

Fig. 1. A section through the gas thermometer furnace (about one-sixth natural size). The bulb is shown in position with the furnace closed ready for heating. The capillary tube connecting with the manometer passes out of the furnace through a packed joint at the upper right-hand corner. The thermoelements pass through the center of the cover as indicated. The water-jacketing is sufficiently complete so that tight joints are readily obtained with ordinary rubber packing.

fixed upon three upright steel rods. The body of the furnace bomb was then arranged to be lowered away from the cover by sliding upon two of the rods so as to expose the bulb and elements for ice and boiling-point determinations before and after each heating. The photograph (fig. 2) shows the furnace body lowered in this way, leaving the bulb free and completely

FIG. 2.

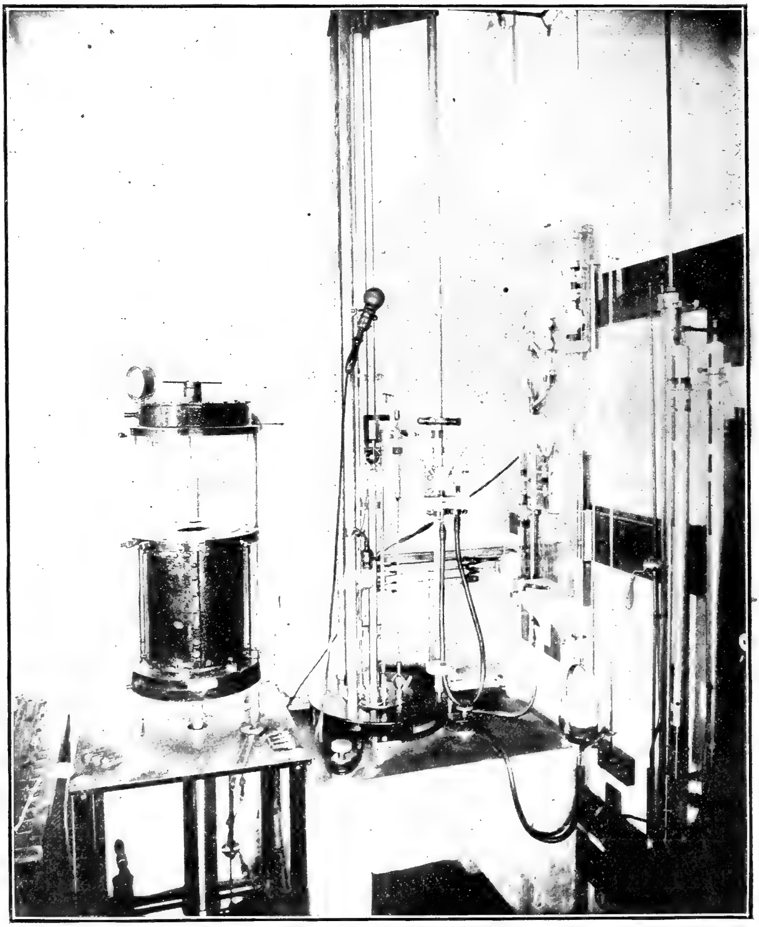

FIG. 2. Photograph of the gas thermometer and accessory apparatus. The gas thermometer measurements contained in the present article were finished in May, 1907. The photograph was taken in July, 1908, after certain details of the apparatus had been changed preparatory to measurement of much higher temperatures. The photograph therefore differs in certain minor details from the diagram (fig. 3) and from the description contained in the text. The apparatus is shown with the furnace open and ready for the ice-point determination.

accessible for arranging an ice bath for the zero reading. Hydraulic power served to raise and lower the furnace conveniently. When the furnace was raised for heating, a circle of bolts provided a positive pressure upon the top joint.

The Manometer.—The manometer was located about $1/2^{\mathrm{m}}$ distant from the furnace and was of the usual U-tube type, constructed with a very heavy cast-iron base and light upper parts in order to render the mercury columns as free as possible from the vibrations of the building. The fixed point to which the mercury level was always adjusted occupied the usual position at the top of the short arm, the other arm extending upward for a distance of about two meters.

The scale, which was 1·8 meters long, was immediately beside the long tube, and was provided with a sliding vernier reading to $0{\cdot}01^{\mathrm{mm}}$. It was of brass with a silver-plated band upon which the divisions were ruled and had been calibrated by the German Normal Aichungskommission in Charlottenburg. The length of any portion of it was known in terms of the German standard meter to the nearest $\cdot01^{\mathrm{mm}}$. The scale was fixed in position below and arranged so as to expand upward through appropriate guides against a rubber cushion with the changes in the room temperature. The long manometer tube also passed through three guide screws at the top of the apparatus, which allowed it to expand and contract unhindered. Readings were obtained by means of two parallel knife edges on the vernier carriage, which could be brought to accurate tangency with the mercury meniscus by a slow motion screw provided for the purpose. The mechanical construction was extraordinarily rigid and very satisfactory. The temperature of the scale and mercury columns was obtained from three thermometers, each set in a short tube of mercury after the manner of Holborn and Day.* Each tube with its thermometer could be moved up and down close beside the scale and mercury columns so as to give the temperature of the top, middle and bottom of the longest column. The observed temperature differences along the mercury column sometimes amounted to 1°. This would not affect the scale length by a dangerous amount, but the average temperature of the mercury column requires to be known to about 0·2°, with the high sensitiveness of this instrument, in order to bring the errors in the pressure determination within the desired limits—hence the three thermometers.

The mercury supply was contained in two basins, one a hollow steel bomb enclosed within the cast-iron base of the instrument, and the other a steel flask mounted upon the wall

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* Holborn and Day, On the Gas Thermometer at High Temperatures, this Journal (4), viii, p. 170, 1899.

FIG. 3.

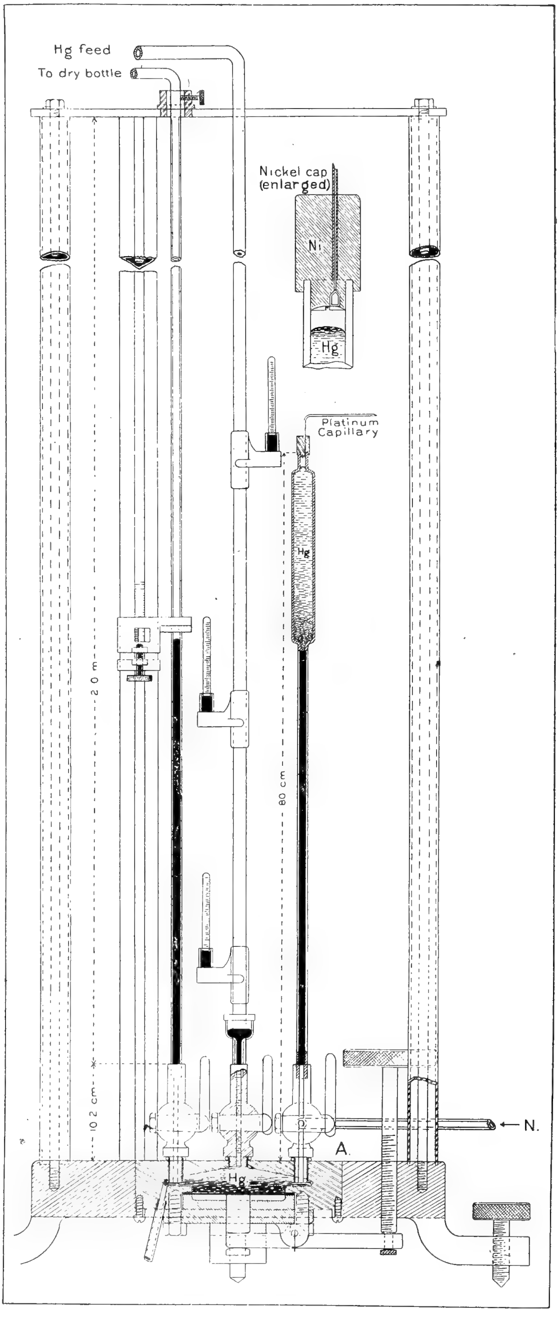

FIG. 3. A diagram of the manometer (about one-eighth size) showing construction and essential features only. Dimensions are approximate.

of the room near the ceiling and connected with the lower reservoir by a flexible iron tube. Cocks conveniently arranged admitted mercury whenever required. The fine adjustment of the mercury level was obtained by the use of a nickel diaphragm which formed the bottom of the lower steel reservoir. This diaphragm was about 12^{cm} in diameter and could be raised slightly by the upward pressure upon its center produced by turning a milled hand screw convenient to the hand of the operator. The lower reservoir was dome-shaped within and opened into a tube and stop-cock at its highest point, through which any air which might chance to become imprisoned within the reservoir might be allowed to escape.

Gas was admitted to the bulb by means of the three-way cock A (fig. 3) leading to a supply of pure nitrogen, the pressure of which could be varied at convenience. It was also possible to exhaust the bulb through the same cock for the purpose of testing for leakage or rinsing the bulb.

Unheated Space.—From the point of view of the errors of the instrument, the most important part of the manometer is the nickel cap at the top of the short arm which carries the fixed point for defining the constant volume. This cap is sealed into the glass manometer tube with ordinary sealing wax of good quality, some care being taken that the sealing wax fills all the cracks, which might otherwise retain gas and become a part of the unheated space. The under side of the cap is hollowed out slightly to conform to the shape of the rising mercury meniscus, and in the center a somewhat rounded point of nickel projects downward about $\cdot 3^{mm}$. When the column of mercury is raised in the arm until it becomes tangent to this point, the constant volume of the system is determined. The setting is made through a fixed magnifying microscope of some twenty diameters power. The portion of the "unheated space" included above the column is about $\cdot 3^{mm}$ thick, 1^{cm} in diameter, and corresponds in form to the mercury meniscus.

The outlet leading to the bulb is a small opening beside the contact point containing a tiny valve of nickel about $1\cdot 5^{mm}$ in diameter and 2^{mm} long, with a ground joint at the top which slides loosely in such a way that if an accidental rise of the mercury column should tend to drive the mercury over into the bulb, this little nickel plug will be lifted by the mercury and automatically close the opening at the ground joint. This tiny valve opens into the capillary ($\cdot 5^{mm}$ diameter) leading outward to the bulb. Fig. 3 will show the construction more clearly. Where the space above the mercury column requires to be reduced absolutely to minimum volume some such protection is essential. If mercury once passes this opening, through accident or oversight, it reaches the bulb almost immediately, and once there, it is a matter of two weeks boiling with nitric acid to get rid of it again.

Even with this valve, it sometimes happened that when gas was bubbled through the mercury in filling, even at the bottom of the tube some 80^{cm} distant from the valve opening, tiny globules of mercury were shot upward with such speed and accuracy of aim as to pass up beside the little valve and into the capillary tube, after which their ultimate destination is inevitably the bulb. The altogether insignificant size of the opening and the distance required to be traversed by such a globule did not convey to us a suspicion that a globule might hit and pass it, but it actually happened on two different occasions, with the consequence of an exasperating delay.

In the present arrangement of the gas thermometer, this accident is also provided against by introducing a gold capillary instead of platinum, between the fixed point and the bulb. Such microscopic globules of mercury are taken up by the gold without reaching the bulb and therefore remain harmless.

Barometer.—It was deemed advisable from the start not to attempt to combine the barometer with the manometer as has usually been done by the French observers. It is a convenient method and is rather necessary if a single observer is to make all the readings, but the combination brings three or four essentially different errors into one reading in a way that does not admit of an intelligent evaluation of their individual magnitudes.

Two barometers were used throughout this investigation, both of Fuess manufacture and of the same type (Wild-Fuess Normal Barometer, 14^{mm} tube). The corrected readings of the two instruments were in perfect accord and were correct in their absolute value within $\cdot05^{mm}$.*

Thermoelectric Apparatus.—The thermoelectric measurements were made with apparatus and by methods which have already been described in varying degrees of fullness in previous publications from this laboratory.†

Briefly, it may be noted in passing that all the thermoelectric measurements without exception were made with platinum-platin-rhodium thermoelements of Heræus manufacture on a potentiometer of Wolff standard construction by direct com-

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* One of these instruments was compared with the normal barometer at the U. S. Weather Bureau at Washington, the other at the Bureau of Standards.

† Day and Allen, The Isomorphism and Thermal Properties of the Feldspars, Publications of the Carnegie Institution of Washington, No. 31, 1905, Allen and White, On Wollastonite and Pseudo-Wollastonite, Polymorphic Forms of Calcium Metasililicate, this Journal (4), xxi, p. 89, 1906; Walter P. White, Potentiometer Installation, especially for High Temperature and Thermoelectric Work, Phys. Rev., xxv, p. 334, 1907.

parison with a saturated cadmium cell. The cell was one of a series described in a previous paper * which has been compared from time to time with the standard cells of the National Bureau of Standards and has never been found to contain an error greater than one or two parts in 100,000. The galvanometer was a Siemens and Halske instrument of the usual moving-coil type. With the help of a small rheostat in series with the galvanometer, the sensibility was maintained at a constant value such that one scale division in the telescope (distant $1{\cdot}5^{m}$ from the galvanometer) corresponded exactly to two microvolts in the thermoelement reading, which is roughly equivalent to one-fifth of 1°. In this galvanometer the wandering of the needle from its zero position was slight and never amounted to more than ·2 or ·3 of a scale division. It was also almost absolutely dead beat with a period of about five seconds, so that adjustments for a temperature reading could be made with extraordinary rapidity and with an accuracy out of all proportion to the needs of the experiment.

The only error to which the thermoelectric observations were subject was the contamination arising from the iridium contained in the bulb. During the first year in which these observations were begun the furnace coil also contained ten per cent of iridium, but at that time the contaminating effect of this metal upon a thermoelement was not well understood. Later on, this coil was exchanged for a coil of pure platinum made especially for this purpose by Dr. Heræus, which was guaranteed to contain no more than 0·05 per cent iridium and which was found upon analysis to contain considerably less than this quantity. Inasmuch as the furnace coil is always the hottest part of the system, this afforded considerable relief, but the position of the elements in contact with the bulb made it impossible to prevent some contamination above 900°, so long as the bulb remained bare. An attempt was made to reduce this difficulty still further by the use of a glaze made from melted mineral albite, which was appreciably soft at temperatures of 1100° but which appeared to prevent the sublimation of iridium so long as the coating remained continuous. The viscous material, however, showed a persistent tendency to gather together into globules, leaving bare spots on the bulb which were not wet by the glaze, so that this protection was not complete. Porcelain insulating tubes open at the end afford little or no protection. We were accordingly driven to the conclusion that for the higher temperatures iridium must be banished from the furnace completely before consistent observations can be obtained. This is the chief reason why

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* Day and Allen, loc. cit. p. 26.

the present series of observations was not extended beyond 1200°. Observations above this temperature will therefore be made the subject of a subsequent paper in which a bulb containing no ridium will be substituted for the one described here.

Up to 1200° our precautions were sufficient to prevent serious contamination of the elements and the error due to such contamination as was unavoidable has been eliminated by frequent calibrations of the three elements throughout the observations, either by comparison with standard elements known to be free from iridium contamination, or with melting point determinations of standard metals. Toward the close of the series, in order to establish absolute proof that the readings were not encumbered with systematic errors, however small, from this cause, an independent observation was made in the following way: The element at the middle of the bulb was replaced by a freshly calibrated new element known to be in perfect condition. After an ice-point determination and with all the precautions above described, the furnace was heated directly and as rapidly as possible to 1200°, where a single observation was made and the furnace immediately cooled down again. The new element was then removed from the furnace and recalibrated in order to establish beyond question the fact that it had suffered no contamination whatever during the short run. This independent determination, in which it was definitely proved that iridium contamination played no part, served to establish the absolute correctness of the high temperature observations in so far as the error from this most persistent source was concerned.

The Gas.—Nitrogen was prepared by dropping a solution of 200 grams of sodium nitrite dissolved in 250 grams of water into a warm solution containing 300 grams of ammonium sulphate and 200 of potassium chromate in 600 grams of water. The gas was then passed through a mixture of potassium bichromate and sulphuric acid and stored over water. Before introducing this nitrogen into the gas thermometer, it was purified by passing it in succession through calcium chloride, hot copper gauze, potassium bichromate in sulphuric acid, two bottles containing potassium pyrogallate solution, sulphuric acid, calcium chloride and phosphorus pentoxide.

No reason has yet arisen in any of the experiments with nitrogen for suspecting limitations of any kind due to the gas. It has shown no tendency to react with the platinum bulb or to pass through its wall or to dissociate at any temperature to which it has yet been carried in gas thermometry. Furthermore Buckingham * has shown by ingenious methods of com-

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* E. Buckingham, loc. cit.

parison that the derivation of the Kelvin thermodynamic scale from the expansion of nitrogen is probably not encumbered with any error of sufficient magnitude to require consideration when compared with the errors and corrections inherent in the experimental measurements. From the standpoint of the underlying theory of the instrument and the interpretation of its results in terms of the thermodynamic scale, a new and extended experimental study of the Joule-Thomson effect is very greatly to be desired, but there is no reason for apprehension in the application of existing data, imperfect and limited as they are. Experimental confirmation of this is contained in the recent work of Jaquerod and Perrot in which the expansion of five different gases (nitrogen, air, CO, CO_2, O_2) between 0° and 1067° was studied in the same bulb under identical experimental conditions. The maximum difference which occurred in any of their measurements was only ·4 of a degree, which is easily within the limits of error of their apparatus.

The Bulb.—The question of a suitable bulb to contain the expanding gas has been and is to-day one of the most serious which gas thermometry confronts. The first experiments (Prinsep) were made with a bulb of gold, which was soon abandoned because of its low melting point. Following this, platinum was employed (Pouillet), but here a difficulty was encountered which eventually caused its abandonment in favor of porcelain on account of its supposed porosity (Deville and Troost, Becquerel). Iodine vapor had been used in the experiments of Deville and Troost as the expanding gas and very high values of several temperature constants in the region of 1000° had been obtained and quite generally accepted, while the much lower values obtained with a platinum bulb with air were discredited for the time. These high values were subsequently shown by Victor Meyer to be due to the dissociation of the iodine, but the controversy resulted in the unfortunate (as it turned out) substitution of porcelain for metal bulbs, a step which was not retrieved for thirty-six years. The porcelain bulb without glaze is porous; with a glaze it is a chemically undefined mineral mixture which not only softens below 1200° with more or less change of volume, but also gives out gas (either original or previously absorbed), so that the porcelain gas thermometer, as it is commonly called, never returned to its original zero after heating to high temperatures.* The uncertainty in the zero which arises through the use of the porcelain bulb causes an error of the order of 5° at 1000°, which is practically impossible of satisfactory correction.

The return to metal bulbs is due to Prof. Holborn of the Reichsanstalt, who has successfully used a platinum bulb (con-

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* Holborn and Day, 1899, loc. cit.

taining 20 per cent of iridium) of 200^{cc} capacity with nitrogen as the expanding gas up to 1600° without discovering any irregularity in its behavior. The porcelain bulb has therefore probably disappeared permanently from gas thermometry. Whether or not some other platinum metal than iridium will not prove preferable with which to give the necessary stiffness to the platinum is a question for the future to decide. It is a matter of great difficulty and some uncertainty to make trustworthy measurements of temperatures above 1000° with platinum thermoelements in the presence of iridium (see paragraph on thermoelectric measurements preceding), even when the iridium is present only in a low percentage (·005) alloy with platinum.

Parenthetically, it may be remarked that the platinum crucibles and other ware as made up for laboratory use in this country are usually stiffened with about 2 per cent of iridium, a quantity amply sufficient to contaminate thermoelements if exposed in the furnace with it to temperatures above 900°.

The Measurements.—The method of procedure with the system in adjustment for observation was then substantially as follows:

With the body of the furnace lowered so as to expose the bulb, a pail of suitable size was brought up about the latter and filled with distilled water and finely divided ice in such a way as to enclose the bulb and so much of the capillary as was included within the furnace when heated. Several readings of the ice point were then made on the manometer, together with simultaneous readings of one or both barometers. To control the expansion coefficient of the gas, these readings were occasionally followed by a second reading at the temperature of boiling water in which the ice pail was replaced by a double-chambered boiling-point apparatus of standard type. In general, however, it may be said that the expansion coefficient of pure nitrogen has already been so carefully determined by Chappuis and others that this observation is superfluous, particularly as the sensitiveness obtainable in a bulb of a size suitable for long ranges of temperature is not sufficient to admit of a determination comparable with theirs.

After the ice point had been determined, therefore, the general procedure was to arrange the three thermoelements in position at the top, middle and bottom of the bulb (fig. 1), to close up the furnace gas-tight and to proceed with the heating. Before turning on the current, however, it was first necessary to exhaust the bomb and to replace the air with a nitrogen atmosphere, the nitrogen being supplied from a separate bomb under high pressure. The nitrogen for this purpose was made in large quantities in the laboratory by the method of Hutton and Petavel,* and pumped into bombs at a pressure of about 1,000 pounds per square inch. One of these bombs could be readily connected with the furnace through appropriate portable connections whenever desired. A pressure gage connecting with the inside of the furnace bomb enabled the pressure within the bomb and outside the bulb to be read at any time. If the advance in pressure outside the bulb did not proceed as rapidly as that within, additional nitrogen could be admitted as required. In general, it can be said of the operation of this arrangement for the adjustment of pressure within and without the bulb, that if the furnace is perfectly tight the two pressures advance together and are never very far apart. Attention to this detail is therefore not burdensome unless the bomb is leaking, in which case the losses must be supplied by the addition of small quantities of nitrogen from time to time. An effort was made to keep the pressure outside the bulb within one-half pound of the inside pressure as read on the manometer.

After the current had brought the temperature to the point where it was proposed to make a reading, about three-quarters of an hour was required to adjust the three resistance coils so as to produce a permanently uniform temperature along the bulb, which limited the number of temperature readings in one working day to six or seven. It was therefore our habit to make readings, at 50° or 100° intervals, so as to cover a considerable range of temperatures each day. On following days intermediate temperatures were selected in such a way that the whole field between 250° and 1200° would eventually be canvassed in steps of 25°. In order to provide a sufficiently rigid control of the conditions within the bulb, however, each day's readings began with a new determination of the ice point.

It is interesting to note in passing that the variation of the ice point after heating, which was a conspicuous feature in all gas thermometric work previous to 1900, has now substantially disappeared with the return to the platinum bulb. Our ice points (column 3, Table II) from day to day showed no disagreement of greater magnitude than that produced by the somewhat irregular contraction of the bulb due to slight variations in the rate of cooling, to which attention has been explicitly called in the chapter on the expansion coefficient of platin-iridium (p. 436).

When the temperature had become constant over the entire length of the bulb, one observer took his position at the telescope of the manometer and the other at the galvanometer, and simultaneous readings were made of the group of ther-

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* Hutton and Petavel, Preparation and Compression of Pure Gases for Experimental Work, Journ. Soc. Chem. Ind., xxiii, Feb. 15, 1904.

moelements and of the pressure within the bulb. Between each two pressure readings a reading of the barometer was made by the observer at the gas thermometer, the barometer having been arranged in a conveniently accessible position for that purpose. All the readings were arranged in symmetrical groups in such a way that the time rate of change of temperature, if any, would fall out in the arithmetical mean of the pressures and temperatures at the beginning and end of the series. At the close of this set of observations, readings were made of the three thermometers which gave the temperature of the mercury column of the manometer. The temperature of the unheated space requires no separate determination in view of the fact that a change of 5° in the room temperature does not affect it by an appreciable amount. The average room temperature was therefore sufficiently accurate to determine the correction for the unheated space.

Following such a series, the temperature was increased by the desired interval and the same operation gone through with again. Constant attention was of course required in the meanwhile to see that, in increasing the temperature of the furnace, and therefore of the bulb, the pressures inside and outside the bulb did not get too far apart. The same was true of the cooling at the close of the series.

Before the bulb was connected up with the manometer for the final filling, readings were made of the position of the fixed point which defines the constant volume upon the scale. This was done by letting in mercury with both tubes open and reading the mercury level in the long tube when the meniscus in the short tube was raised so as to be just tangent to the fixed point. The following readings were obtained:

POSITION OF "FIXED POINT" ON THE SCALE.

May 9, 1906

		Temperature of Scale	
	Scale reading cm	Lower end Thermometer No. 15	Upper end Thermometer No. 11
	69·049	22·4°	22·8°
	·050	22·5	23·0
	·051	22·5	23·1
	·053	22·7	23·4
	·054	22·6	23·6
	·055	22·6	23·7
	·054	22·6	23·7
Mean	69·0523	25·56	23·33
Correction	—·001	—0·3	—0·45
	69·051	22·26	22·88
	69·051		22·57°

On account of the unequal expansion coefficients of the (brass) scale, and of the (glass) manometer tube, in which the fixed point is mounted, the elevation of the fixed point with respect to the scale will change with temperature. The variation amounts to $-0{\cdot}0009^{\text{cm}}$ per degree rise in temperature.

Volume of Bulb.—The volume of the bulb, including the stem, was determined by weighing with water at the beginning of these experiments and again at their conclusion with the following results:

Volume of bulb and stem,	Sept. 1905	$195{\cdot}79^{\text{cc}}$
" " " "	Feb. 1908	$195{\cdot}66^{\text{cc}}$

Since V_0 enters into the computation of temperature only as a part of the correction factor for the unheated space, and as this total correction is never more than 5°, it is obvious that the absolute volume of the bulb is not, of itself, an important factor in the problem. On the other hand, the correction for the expansion of the bulb with the temperature amounts to 45° at 1100°, and is the most important correction factor which requires to be determined. An error of 1 per cent in the determination of this constant (β) produces an error of 0·5° at 1100°.

*Expansion Coefficient of the Bulb.**—The determination of the expansion coefficient of the bulb did not prove to be the perfunctory operation which had been anticipated, but developed into an independent research of somewhat exasperating character, covering several months.

There are two methods which might be pursued to obtain this constant. It is theoretically possible to determine the actual volume expansion of the gas thermometer bulb in position in the furnace, but an effort to carry it out experimentally a few years ago developed serious difficulties where the range of temperature is so great and the accuracy required so considerable. We therefore preferred to obtain a bar made from the same material as the bulb, and to determine its linear expansion under conditions which were under more perfect control.

In principle, the method of procedure is the one used at the Reichsanstalt. A bar of platin-iridium 5^{mm} in diameter and slightly more than 25^{cm} in length was prepared for the purpose and heated in a tube furnace in which the temperature could be maintained nearly uniform from one end of the bar to the other and conveniently regulated up to 1000° or more. The ends of the bar were filed flat for a distance of 6^{mm} and upon these flat surfaces millimeter divisions were ruled with a dividing engine. The balance of the apparatus consisted of a pair of micrometer telescopes mounted so as to

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* By A. L. Day and R. B. Sosman.

observe these divisions and also to maintain a constant distance between the fixed cross-hairs from beginning to end of the experiment. Heating the bar then served to move the ruled lines past the fixed cross-hairs of the telescopes and the amount of the displacement was measured for any desired temperature.

Fig. 4.

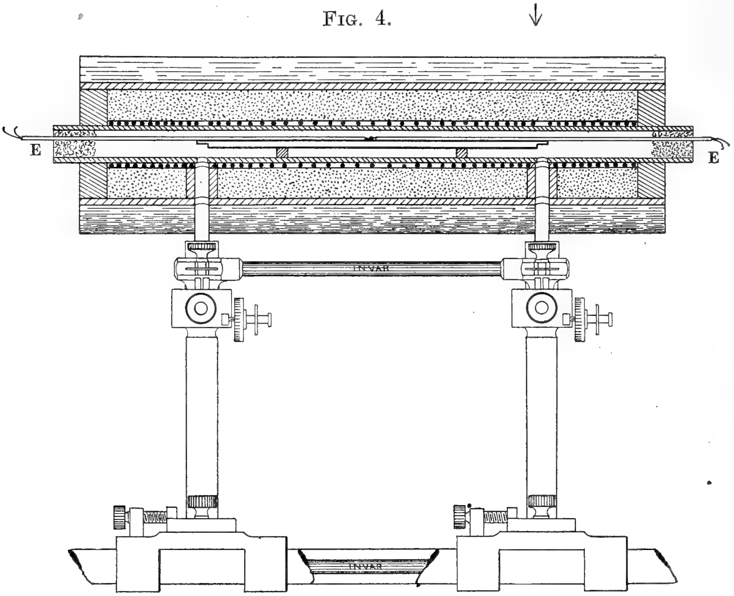

Fig. 4. Section through furnace showing bar, thermoelements (E,E) and microscopes in position. A section through the arrow is shown in fig. 5.

The aggregate expansion of a 25^{cm} bar over the interval from 0° to 1000° is about $2·5^{mm}$. The telescope micrometers as they were focused for the measurements gave about 450 divisions (each about 2^{mm}) of the drum for one millimeter on the bar, and in the individual readings differences of ·2 or ·3 of a division were readily distinguishable. It was therefore easily possible to make very accurate measurements of the expansion of such a bar by direct observation without the use of a contact lever or any multiplying device whatsoever.

The essential features of the apparatus can be partly seen from the figures and partly require some description. The furnace was erected on a separate stand quite independent of the measuring apparatus. It consisted of a narrow tube wound with a heating coil and containing, opposite the ends of the bar, two small openings through which the divisions could be seen. The inside diameter of the tube was about 2^{cm}, and the side openings, narrow slits about 3^{mm} in width by 10^{mm} long. The tube and its heating coil extended some 10^{cm} beyond the ends of the bar and the wire was wound somewhat more closely at the ends than in the middle to counteract the cooling effect of the end and side openings. In this way a reasonably uniform distribution of temperature along the bar was secured.

The first furnace tube was of porcelain wound with nickel wire 1^{mm} in diameter, the separate turns being insulated from each other with a magnesite cement which is sufficiently refractory and conducts but little at any temperature which the nickel wire can withstand. Thus arranged, the heating coil was mounted horizontally in a much larger tube (8^{cm} diameter) of porcelain and the space between filled with dry calcined magnesia of good insulating quality. The whole was water-jacketed throughout in order to prevent any heat from the furnace from entering the optical system and disturbing the fixed distance between the micrometers upon which the accuracy of the measurement absolutely depends. Both the insulating material and the water jacket were provided with small openings corresponding to the slits in the furnace tube so that the bar could be illuminated and observed from without.

Fig. 5.

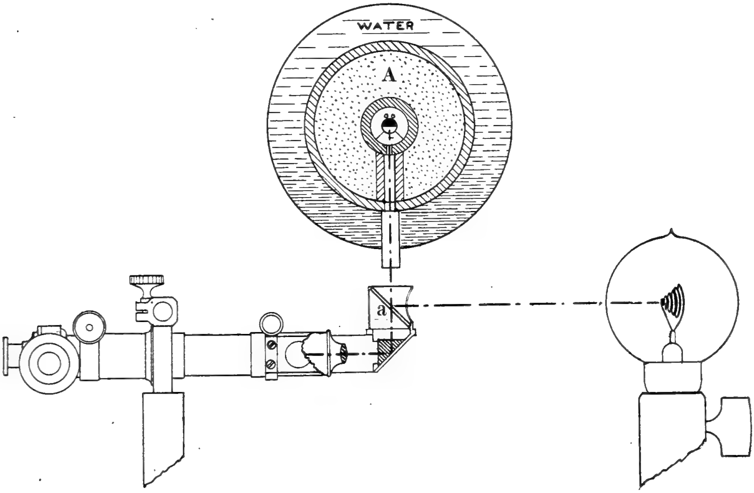

Fig. 5. A section through the furnace (A) at one of the openings showing method of illumination by 45° plane glass plate (*a*). The bar and thermoelement appear in position though not well shown by this section.

The measuring portion of the apparatus was entirely separate from the furnace and consisted of two telescopes, mounted upon upright brass tubes firmly secured in position upon massive brass carriages which slid freely upon horizontal steel guide bars some 4^{cm} in diameter and ground true. The two carriages were then connected by an invar metal bar (fig. 4) to which they were stoutly and permanently clamped. The whole system was then free to move upon its guides, but the relative position of the telescopes was fixed. The object of this arrangement was obviously to secure a constant distance between the telescopes, in spite of slight changes in the temperature of the system due to the temperature of the room or the heat from the observer's body, whatever the relative expansion of the various parts of the apparatus. After a good many observations had been made, it was found that the upright brass tubes supporting the telescopes upon their carriages were not uniformly affected by the heat from the body of the observer. They did not therefore expand uniformly and parallel to each other, but tended to buckle very slightly during each series of observations. This was subsequently corrected by a second invar bar above the telescopes which in combination with the first formed a rugged rectangular system which preserved the cross-hair distance without change throughout long series of observations.

In mounting the furnace for observation, the side openings which gave access to the scale divisions were directed downward in order to reduce to a minimum the convection currents of air which endanger the constancy of the temperature within. The openings were also made as small as possible for the same reason. It therefore became something of a problem to bring in light enough to illuminate the scale divisions and at the same time to make observations of the change in length with the temperature. The device adopted was this: In the optical axes of the telescopes and some 5 or 6^{cm} beyond the objective, small total reflecting prisms were mounted upon the extended telescope tubes in such a way as to deflect the line of sight at right angles and upward into the furnace. Above these prisms and between them and the furnace (see fig. 5), windows of plane optical glass were set at 45° in such a way that they served to reflect the light from an incandescent lamp upward from their outer surfaces without materially interrupting the line of observation through the telescope and total reflecting prism. By this device the path of the illuminating light was the same as the path of the reflected light which reached the observer, which served to give plenty of illumination for the scale without increasing the size of the openings beyond what was required to see the actual expansion and to measure it.

The illumination was provided by a single incandescent lamp of 100 candle power with a spiral filament of stock type giving an intense and concentrated illumination. It was mounted behind the furnace some 20^{cm} distant from the openings, and was so screened that its heat did not reach the

FIG. 6.

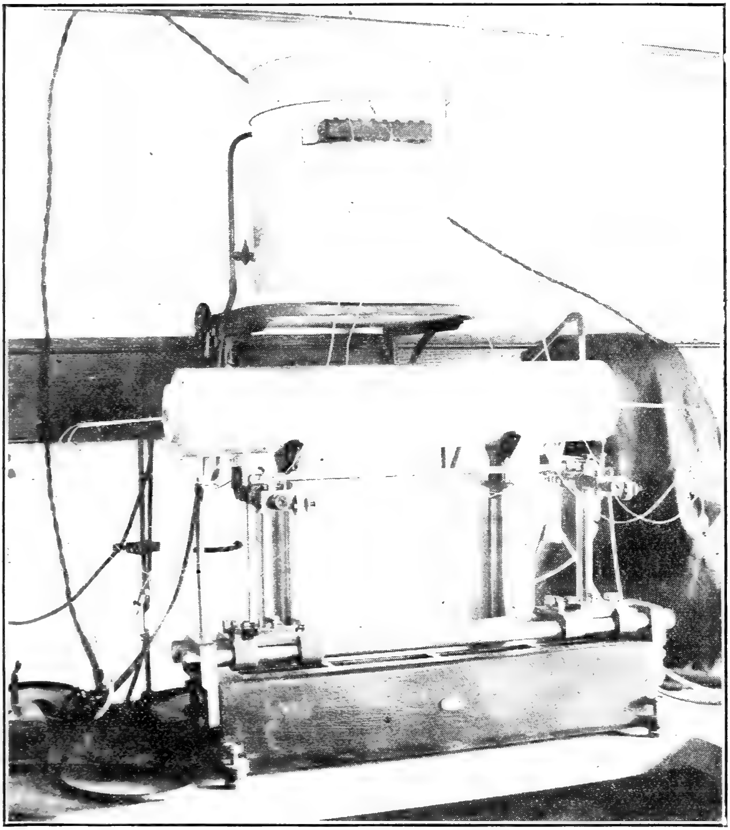

FIG. 6. The expansion apparatus. A photograph of a furnace and accessory apparatus for the determination of expansion coefficients over long ranges of temperature. The illustration represents a later form of apparatus than that described in the text. The difference lies mainly in the increased length; the present furnace is arranged to take bars 50^{cm} long instead of 25^{cm} as described.

optical parts of the apparatus save in the two beams which enter the furnace for the illumination of the bar.

The temperature of the bar was determined at first with one thermoelement and afterward with two, which entered the furnace tube from opposite ends in such a way that their hot junctions could be bound together and moved freely along the bar and in contact with it, in order to give a double reading of the temperature at any point desired. In this way we obtained the actual distribution of temperature along the bar corresponding to each determination of its length.

To complete the system, a standard brass bar was prepared of the same size and shape as the platin-iridium bar under investigation, but with silver surfaces let in at the ends to carry the divisions. This bar was compared at 20° C. with the standards of length at the Bureau of Standards, and served to establish the absolute distance separating the cross-hairs before and after each set of observations.

The method of procedure was now substantially as follows: The standard brass bar was placed in position in the furnace at the temperature of the room. All the necessary adjustments to secure good illumination, to bring the cross-hairs parallel to the scale divisions, and to bring the lines into sharp focus, were then made once for all, and these adjustments were never again disturbed until the series was completed. The field of the microscopes included 5^{mm} of the bar, but only the three scale divisions bounding the 2^{mm} nearest to the fixed cross-hair were used. Toward the close of the investigation, for an important reason which will presently appear, only the two bounding divisions of the single millimeter which included the fixed cross-hair were read and all the observations which had been made outside this limited region were rejected. Readings were made from left to right in each microscope and then repeated in the reverse direction to obviate errors from the micrometer screw. The temperature for this measurement was determined with a glass thermometer thrust into one end of the furnace tube adjacent to the bar and read before and after the series of micrometer readings. This observation served to establish in absolute measure the distance apart of the fixed cross-hairs of the microscopes. The brass bar was then removed and the platin-iridium bar corresponding to the gas thermometer bulb inserted in its place in the same relative position. It is necessary here again to emphasize the fact that all further adjustment must be made with the bar and not with the optical parts of the apparatus.

Having brought the bar into exactly the same position with respect to the telescopes which the brass bar previously occupied, and having introduced the thermoelements in such a way that their hot junctions were free to travel along the bar from end to end without disturbing it, a second series of observations at the temperature of the room was made in the same way as before. This yields the absolute length of the bar at room temperature in terms of the standard brass bar. The furnace is then ready for heating to the temperatures desired.

In the determination of the high temperature scale carried out at the Reichsanstalt in 1900, four observations of the expansion of the bulb material (250°, 500°, 750° and 1000°) were deemed sufficient, and it was not thought necessary in our earlier observations to increase this number materially. We therefore began with a 200° interval. After the observation at the temperature of the room, the bar was accordingly heated to 200° C. and sufficient time (about 30 minutes) allowed for the temperature to become constant throughout the furnace, after which a temperature reading was made at the middle of the bar with each element. Observations of length were then made in the same order as before upon the pair of lines adjacent to the fixed cross-hair in each of the microscopes, followed by a second temperature reading at the middle of the bar. After these observations of length and before any change was made in the temperature, nine consecutive pairs of observations were made of the temperature distribution along the bar, first at the center, then on the left section at 5, 10 and 12^{cm} out from the middle, then the center repeated; then upon the right section with similar intervals, and again the center—all with both elements. By this means an accurate measurement of the temperature along the bar corresponding to the length measurement just completed was obtained. The whole procedure was then repeated at temperatures of 400, 600, 800 and 1000° C.,* after which the furnace was allowed to cool over night and the length of the bar at the temperature of the room again determined. Immediately following this an observation of the brass bar was made in order to establish the fact that the distance separating the cross-hairs had not been accidentally disturbed by the manipulation of the furnace during heating.

At 800° and 1000° the bar is self-luminous to a sufficient extent to enable measurements to be readily made without outside light, but it was deemed advisable to use the outside light in the same way at these temperatures also. In passing from outside to inside illumination, the lines are at first dark on a bright ground, and then bright on a dark ground, a change to which the eye accustoms itself only with considerable difficulty. The measurements were therefore much more uniform when outside light was used throughout.

The measurements of the temperature at once encountered the difficulty that the exposure of the thermoelement in the presence of iridium at a temperature of 1000° contaminates it by an amount sufficient to cause a small but cumulative error. This exposure was necessary with the apparatus as we had

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* Subsequently, when we had reason to suspect an irregularity in the rate of expansion, these observations were repeated every hundred degrees and then every fifty degrees in the region between 600° and 1000°.

arranged it, and there was therefore nothing to do but to make the time of the exposure as short as possible, and by the use of two elements fastened together and extending out of the furnace at opposite ends, to so arrange the conditions that any contamination, if sufficient to affect the temperature, would become immediately apparent. As W. P. White of this laboratory has shown in a recent paper,* the most critical portion of a thermoelement is not the portion along which the temperature is constant, but the region where the element passes from one temperature to another. In our furnace, for example, the region of exposure to constant temperature could give rise to no error of reading however much the element might be contaminated in that region, but if a contaminated portion of the element were at any time to come into the region lying between the end of the bar and the outside of the furnace an immediate difference in its reading should become evident. It was therefore arranged that the junctions of two elements should be bound together so as to record the temperature of the same point within the furnace and that whenever this combination of two elements was moved toward one end of the bar or the other, that a greater length of one of the elements should be exposed within the furnace than of the other. If there is contamination a difference in reading between the two elements will be immediately conspicuous. In the earlier observations comprising this investigation, only one element was used, and by way of control at the close of a long series of observations a second element was introduced in the manner indicated above. It then became immediately evident that the first element had become contaminated and that the observations made with it were affected to a degree which could not be established after the observations themselves were over, and which therefore necessitated the rejection of several entire series. This misfortune may serve to emphasize the necessity of using more than one thermoelement in all cases where it is possible to do so.

Three other difficulties were met with which proved to be sources of considerable inconvenience, and which serve in greater or less degree to place limits upon the accuracy attainable in this particular apparatus. The first was the temperature gradient along the bar, of which mention has already been made. Earlier observers have sometimes been content in similar cases to heat a bar with the electric furnace and to make their measurements upon cold projecting ends, that is, under conditions such that the actual temperature along the bar varies from the temperature of the room to a maximum near the middle of the bar. The resulting temperature to

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* Walter P. White, Phys. Rev., xxvi, p. 535, 1908.

which a given measured length is then referred, is an integral of a temperature range which varies all the way from that of the room to some point considerably higher than that for which the length measurement is recorded. This situation seems to us to comport badly with the accuracy otherwise attainable in measurements of this kind, if not to violate fundamental definitions. Unless the expansion coefficient can be treated as linear, such a determination is obviously only an approximation. Furthermore there is ample precedent for anticipating inversions in an alloy of this character such that the expansion coefficient of the material below the inversion temperature would differ considerably from that above it. An integration, therefore, in which the temperature range is large may well overlap two physical states in such a way that the length measurement loses all significance. We have not been able to establish the fact that such an inversion exists in the 10 per cent platin-iridium alloy within the temperature range over which these measurements were made, although there is an obvious break in the continuity of the expansion, of small magnitude, which recurs with some persistence, as can be seen from the tables which follow (pp. 437 *et seq.*).

Supposing such an inversion to exist, it would of course follow that the expansion would be a discontinuous function of the temperature, a separate expansion coefficient would require to be determined above and below this point, and the two would not bear any necessary relation to each other. If such a situation exists in the present bar, the difference is so small as to be negligible for our present purpose, but the plain indication of an irregularity led us to appreciate the necessity of maintaining the bar as nearly constant in temperature as possible during the length measurements in order to enable us to interpret the measurements intelligently.

The problem of accomplishing this result gave us considerable anxiety. As has been stated above, the scheme of making optical measurements directly upon the bar without multiplying device of any kind necessarily involves an opening in the furnace coil opposite each end of the bar, and a consequent cooling of that portion of the bar which is opposite the opening. The amount of this cooling, which is greatest at the highest temperatures, reached a value of about 4 per cent in the first furnace coil which we wound. The temperature distribution along the bar is measurable with any accuracy desired by moving the thermoelements about, or its effective average can be determined by direct integration with a platinum resistance thermometer of equal length, stretched parallel to the bar. We chose the former method on the ground that it yielded more information, and then sought in addition to diminish the irregularity as much as possible for the reason given above. Accordingly, another furnace coil was wound with the turns closer together near the openings. This changed the temperature gradient considerably without materially improving it (see Furnace II seq.), after which a third coil was prepared with still closer windings, which proved to be considerably overcompensated and was rejected. In all, we made five separate trials of this kind, in the last two of which (Furnaces III and IV) a thick-walled iron tube was substituted for the porcelain furnace tube in the hope of gaining increased uniformity of temperature through the increased heat conductivity of the tube itself. This arrangement succeeded better, but we found it impossible to so arrange a winding that the temperature opposite the openings was uniform with that at the middle of the tube for all temperatures between 0 and 1000°.* A winding which gave good results at the lower temperatures gave insufficient compensation at the higher ones. The obvious possibility of reaching a uniform distribution by subdividing the coil into sections in each of which the current could be independently varied was not tried on account of the cumbersome manipulation required, and in part also because the results which we obtained with considerable differences in the gradient appeared to agree very well among themselves.

The temperature carried out in the tables in each case represents the integral of the nine pairs of readings described above. The actual error which enters into an observation from the variation in temperature opposite the openings is therefore the error in establishing this integral, which can hardly be greater than 1° C. or ·1 per cent.

It will probably occur to other experimenters, as it did to us, that this difficulty with the exposed ends of the bar is due in part to the unavoidable air currents circulating through the small openings, and that these ought to be checked by the introduction of windows. We made two attempts to reach the difficulty in this way, first using quartz windows set in the opening of the furnace tube itself and therefore heated with the tube; and second, by the use of glass windows set in the water jacket and therefore outside of the heated zone. The quartz windows behaved very well until high temperatures were reached, when they become displaced by the unequal expansions in the apparatus, thereby causing displacements in the apparent position of the lines of the scale. When the windows

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* A considerable part of the difficulty in correcting the irregular furnace temperature was due to the instability of nickel wire at the higher temperatures. The oxidation is so rapid that a favorable arrangement of the windings, when obtained, does not give uniform results for more than one or two series of observations. It is our purpose to abandon it in favor of a nickel-chromium alloy or pure platinum.

were removed to the colder parts of the furnace in order to avoid this displacement, sufficient water vapor condensed upon them from within to obscure the field, so that the window scheme had to be entirely abandoned.

The second considerable difficulty to be encountered was due to the effect of the outside illumination of the divisions of the bar in a field of rather high power (about 25 diameters). Consider the bar to be illuminated by a beam of light from a fixed source (which remains constant in position while the bar expands) and the light received through the telescope into the eye to be reflected from the polished parts of the bar surface between the rulings. For reasons which appear in the adjacent figure (fig. 7), this reflected light does not show the lines to be equally* displaced after expansion. The reason for this is plain after a brief consideration. If lines are ruled with a sharp tool upon soft platinum metal which is afterward polished to remove the burr left by the cutting tool, the effect is to round off the two edges of each cut to a greater or less extent, and thereby to present approximately cylindrical bounding surfaces to the incident light. The apparent boundary of the line will then be defined by the reflection of this light from the cylindrical surface into the telescope. Now, if this cylinder be moved laterally in the direction produced by the expansion, the light will be reflected from a different point on the

Fig. 7.

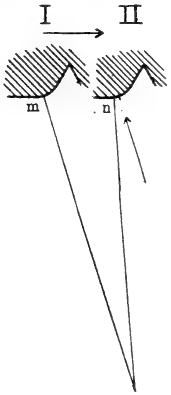

Fig. 7. Showing how the lines appeared displaced after expansion. Actual expansion, *m* to point indicated by the arrow. Apparent expansion, *m* to *n*.

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* The small expansions of the millimeter sections themselves have been taken into account, although not explicitly mentioned in this discussion.

cylinder and will therefore show the line in a somewhat different apparent position from that which would be produced by the expansion alone. The drawing is purposely exaggerated to show exactly the character of this optical error. It was our habit in beginning these observations to select three appropriate lines upon each end of the bar, and to make all the measurements on these, whereupon it was found by a careful examination of the results that the displacement of the three lines after expansion differed systematically by a measurable amount and in a manner which could not be accounted for by the movement of the bar. This difference was very puzzling for a long time, but was finally traced to the source described, and this inference verified by actually moving the bar about in the field in various ways without changing the temperature. The consequence of this discovery was to compel the rejection of all measurements made upon lines other than those immediately adjacent to the fixed cross-hair in the center of the field. The number of observations at each end was therefore reduced to two, but the agreement of the results was very considerably increased thereby.

The third and most serious difficulty of all amounts to an essential limitation of the material itself and is therefore not dependent upon the method of measurement. It is the failure of the bar to return to its initial length after heating.

In this particular bar, 25^{cm} in length, we actually found differences between the lengths before and after heating of the order of magnitude of $\cdot 02^{mm}$, which varied from one series of experiments to another according as the bar happened to be cooled rapidly or slowly. This quantity is some fifty times larger than the smallest magnitude we could measure, and inasmuch as it depends only upon measurements at the temperature of the room, is readily accessible. It is of course immediately obvious that this constitutes a limitation upon the accuracy of gas-thermometric measurements in a bulb of this material, but in this very particular the behavior of platin-iridium is enormously more favorable than that of any of the other materials (porcelain, fused silica) which have yet been applied to this purpose. Although this limitation of platin-iridium would not therefore alone be sufficient to deprive it of continued usefulness for the gas-thermometer, yet when combined with the contaminating action of the iridium which distils out of the alloy at all temperatures above 900° in sufficient quantities to eventually destroy the accuracy of the thermoelement, it has led us to abandon the iridium alloy for the future, and to substitute an alloy of rhodium.

This study of the irregularities present or possible in the expansion of the bulb was pursued much more persistently than is usual in an investigation which is but incidental to a much larger one, on account of the unexpected values obtained. The expansion of pure platinum as determined by Holborn and Day* is given by the equation,

$$\lambda = (8868\, t + 1{\cdot}329\, t^2)\, 10^{-9}$$

while that of platinum, containing 20 per cent iridium, made in the same furnace at the same time, gave

$$\lambda = (8198\, t + 1{\cdot}418\, t^2)\, 10^{-9}.$$

We had expected, as Holborn and Day assumed in their calculations in 1900, that the expansion of the 10 per cent alloy ought to fall approximately between the two. When it therefore became apparent that our observations were leading to a value for the 10 per cent alloy which was of the same order of magnitude as that hitherto found for pure platinum, we were for a long time quite unwilling to accept the result. After the close scrutiny of the apparatus and its limitations described above, all of which, either singly or in combination, appeared totally inadequate to account for the unexpected expansion coefficient obtained, there remained the single possibility that some confusion had arisen in the preparation of the bar; but Doctor Heræus, who made the bar, would not admit this possibility. Even then, it was deemed wise to make a chemical analysis of the bar itself, and this was done by E. T. Allen of this laboratory, with the result that the iridium content was found to be 10·6 per cent. There appears therefore no further alternative but to accept the irregular variation of the expansion with the percentage composition as characteristic of platin-iridium, following the well-known example of the iron-nickel alloys.

The observations follow:

IN FURNACE I.

Temperature Distribution along the Bar.

Left			Middle (Corrected Temperature)	Right		
12cm	10cm	5cm		5cm	10cm	12cm
+10°	+11°	+ 7°	287·7°	− 4°	−13°	−15°
+12	+13	+ 7	511·2	− 2	−15	−24
+10	+23	+13	700·	− 5	−21	−30
+28	+33	+17	1044·1	−11	−31	−46

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* On the Expansion of Certain Metals at High Temperature, this Journal (4), xi, p. 374, 1901.

Expansion.

Date	Corrected Temperature	λ/L		Obs.—Cal.
		Observed	Calculated	
Dec. 30, 1907	287·7° *	·002635	·002661	−26
	511·2	·004871	·004879	− 8
	712·9	·007051	·006994	+57
Dec. 31, 1907	700·0	·006878	·006855	+23
	866·6	·008653	·008677	−24
Jan. 2, 1908	504·0	·004812	·004805	+ 7
	504·4	·004813	·004810	+ 3
	690·0	·006763	·006748	+15
	689·4	·006755	·006742	+13
	856·5	·008600	·008565	+35
	856·4	·008610	·008564	+46
	1044·1	·010616	·010699	−83
	1043·8	·010635	·010695	−60

$\frac{\lambda}{L} = \frac{\text{total expansion}}{\text{initial length}}$ Equation used for the "calculated" expansions, $\lambda = (8869{\cdot}5t + 1{\cdot}3192t^2)10^{-9}$

IN FURNACE II.

Temperature Distribution along the Bar.

Left			Middle	Right		
12cm	10cm	5cm	(Corrected Temperature)	5cm	10cm	12cm
−13°	− 1°	0°	294·0°	−4°	−12°	−27°
−22	− 6	− 2	392·0	−6	−20	−41
−28	− 9	− 4	491·0	+2	−17	−33
−30	−13	− 5	592·5	0	−10	−30
−34	−15	− 5	695·0	+4	− 3	−27
−35	−17	− 7	795·0	+8	+ 4	−17
−52	−21	− 9	894·0	+9	+ 6	−12
−51	−21	−10	994·0	+8	+ 8	−14

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* Inasmuch as the expansion-coefficient which is here being determined itself enters into the determination of the temperature, the two quantities are not independently variable. The temperatures given above are, therefore, based upon tentatively assumed constants which have been chosen about where the final values were expected to come. The assumed data are these:

Zinc melting point	419°
Silver " "	960
Copper " "	1083

With actual temperatures 1° higher or lower, the expansion coefficient would not be affected by an amount equal to one-tenth of one per cent in any part of the curve. The assumed values are, therefore, amply exact for the purpose.

Expansion.

Date	Corrected Temperature	λ/L		Obs.—Cal.
		Observed	Calculated	
Feb. 25, 1908...	294·0°	·002679	·002692	−13
	392·0	·003665	·003638	+27
	491·0	·004660	·004619	+41
	592·5	·005632	·005651	−19
	695·0	·006657	·006719	−62
	795·0	·007741	·007788	−47
	894·0	·008848	·008871	−23
	994·0	·010086	·009991	+95

Equation used for the "calculated" expansions,

$$\lambda=(8778{\cdot}6t+1{\cdot}2801t^2)10^{-9}$$

In Furnace III.

Temperature Distribution along the Bar.

Left			Middle	Right		
12^{cm}	10^{cm}	5^{cm}	(Corrected Temperature)	5^{cm}	10^{cm}	12^{cm}
− 2°	− 1°	− 0°	297·9°	− 1°	− 5	− 7°
− 6	− 3	− 1	397·3	− 1	− 5	− 8
− 9	− 6	− 2	496·3	− 1	− 5	− 9
−13	−10	− 3	594·3	+ 1	− 3	− 7
−16	−12	− 4	646·9	+ 2	− 2	− 6
−16	−12	− 4	646·6	+ 2	− 2	− 5
−17	−13	− 4	697·0	+ 2	0	− 4
−19	−14	− 5	747·8	+ 4	+ 2	− 2
−23	−17	− 6	796·3	+ 5	+ 3	0
−27	−20	− 7	846·2	+ 6	+ 5	+ 1
−26	−20	− 8	897·2	+ 6	+ 8	+ 4
−29	−23	− 9	946·6	+ 7	+11	+ 8
−31	−25	− 9	1001·5	+11	+17	+14

Expansion.

Date	Corrected Temperature	λ/L		Obs.—Cal.
		Observed	Calculated	
Apr. 6, 1908 ...	297·9°	·002770	·002759	+11
	397·3	·003739	·003730	+ 9
	496·3	·004720	·004723	− 3
	594·3	·005714	·005732	−18
	646·9	·006267	·006283	−16
	646·6	·006262	·006280	−18
Apr. 8, 1908 ...	697·0	·006800	·006815	−15
	747·8	·007346	·007360	−14
	796·3	·007897	·007888	+ 9
	846·2	·008445	·008437	+ 8
	897·2	·009013	·009005	+ 8
	946·6	·009579	·009561	+18
	1001·5	·010206	·010187	+19

Equation used for the "calculated" expansions,

$$\lambda=(8874{\cdot}4t+1{\cdot}2889t^2)10^{-9}$$

IN FURNACE IV.

Temperature Distribution along the Bar.

Left			Middle	Right		
12^{cm}	10^{cm}	5^{cm}	(Corrected Temperature)	5^{cm}	10^{cm}	12^{cm}
− 3°	− 2°	0°	299·1°	− 1°	− 4°	− 5°
− 5	− 3	0	399·2	− 1	− 4	− 6
− 9	− 5	− 1	497·0	− 1	− 5	− 7
−14	− 9	− 2	598·3	0	− 3	− 6
−16	− 9	− 3	648·0	+ 1	− 1	− 5
−19	−12	− 4	709·5	+ 3	0	− 4
−21	−15	− 4	748·7	+ 4	+ 2	− 3
−25	−18	− 6	799·1	+ 6	+ 4	− 1
−30	−22	− 7	846·1	+ 7	+ 6	+ 1
−30	−22	− 8	900·4	+ 8	+ 9	+ 4
−36	−26	−10	949·6	+10	+13	+ 7
−36	−27	−11	1000·5	+12	+17	+11

Expansion.

Date	Corrected Temperature	λ/L		Obs.—Cal.
		Observed	Calculated	
Apr. 17, 1908...	299·1°	·002763	·002755	+ 8
	399·2	·003750	·003730	+20
	497·0	·004697	·004708	−11
	598·3	·005702	·005748	−46
	648·0	·006265	·006268	− 3
	709·5	·006889	·006921	−32
	748·7	·007344	·007343	+ 1
	799·1	·007897	·007890	+ 7
	846·1	·008423	·008407	+16
	900·4	·009018	·009011	+ 7
	949·6	·009585	·009566	+19
	1000·5	·010160	·010146	+14

Equation used for the "calculated" expansions,

$$\lambda = (8814{\cdot}1t + 1{\cdot}3260t^2)10^{-9}$$

The mean of the equations derived from the observations in the four furnaces, each weighted according to the number of observations in that particular series, is

$$\lambda = (8841\,t + 1{\cdot}306\,t^2)\ 10^{-9}$$

which is the equation used to compute all the gas-thermometer observations.

This interpolation formula is a simple equation of two coefficients obtained by the method of least squares, giving equal weight to all the observations.

Inasmuch as no one of the differences between observed and calculated values reaches 1 per cent in value, this form of equation, which has been frequently employed for the purpose, is perhaps as well adapted to represent the experimental data as another. After it was discovered that the bar after heating did not return to its initial length, but varied within considerable limits from one heating to another, it became apparent that if the contraction upon cooling was not uniform, the expansion on reheating was probably also irregular to the same degree, and that the room temperature observations could not be expected to follow this or any other simple equation very consistently. That such irregularities exist and attain such magnitude as seriously to limit the power of any simple formula to reproduce the expansions over the whole range will be immediately apparent from an examination of the columns of differences (Obs.—Cal.). It is more directly observable in the experimentally determined values of the expansion between 0 and 300° taken from the four series which have just been given.

Measured Expansion in Millimeters
between 0 and 300°.

Dec. 30, 1907	0·687^{mm}
Feb. 25, 1908	0·681
Apr. 6, 1908	0·700
Apr. 17, 1908	0·696

By way of experiment we tried an equation of three coefficients on the last two series, both of which contain observations at 50° intervals, omitting in each case the room temperature observation in which the irregularity in the expansion itself chiefly appears, and found it possible to reproduce the measured behavior of the bar in the region from 300° to 1000° with differences less than one-fifth as large as those recorded in the tables above. There is, therefore, abundant evidence that the uncertain region is confined to the lower temperatures and that the higher temperatures have so far offered no serious difficulty or irregularity, either in measurement or convenient representation. The expansion measurements over the entire range from 0° to 1000° are probably in error by about 0·5 per cent, most of which is directly attributable to these irregularities in the behavior of the metal at the lower temperatures. In the gas thermometer this corresponds to about 0·25° at 1000°.

This uncertainty in the expansion of the metal at low temperatures appears in the gas thermometer data as a difference, from one day's observations to another, in p_0,—the pressure of the gas at 0°,—which will be found to vary irregularly within narrow limits.

The Pressure Coefficient of Nitrogen.—A number of determinations of the pressure coefficient of nitrogen, under different initial pressures, were made by observing the pressure inside the bulb when it was immersed alternately in ice and in steam, and with the following results:

Initial Pressure	$a = \frac{p_{100} - p_0}{100}$	No. of Observations
314^{mm}	0·003665	4
550	·003668	5
744	·003670	6
985	·003673	12

Chappuis has obtained the following values of a:

Initial Pressure	$a = \frac{p_{100} - p_0}{100}$	
529^{mm}.	0·00366811	Traveaux et Mémoires du Bureau International des Poids et des Mesures, vols. 6 and 12.
533	·00366846	
793·5	·00367180	
995·95	·00367477	

Computation of Results.—The formula for the constant volume gas thermometer may be written in the form,

$$\frac{pV}{1+at} + \frac{pv_1}{1+at_1} + \frac{pv_2}{1+at_2} = p_0V_0 + \frac{p_0v_1}{1+at'_1} + \frac{p_0v_2}{1+at'_2}$$

In this equation:

V_0 = volume of bulb at 0° .... $195{\cdot}547^{cc}$.
V = volume of bulb at $t°$.
p_0 = initial pressure, i. e., pressure when bulb is at 0°.
p = pressure at temperature of $t°$.
v_1 = portion of "unheated space" enclosed in furnace (in which temperature varies from the temperature of the bulb to that of the room) .... $0{\cdot}161^{cc}$.
v_2 = portion of "unheated space" outside of furnace .. $0{\cdot}128^{c}$.
t_1 = estimated mean temperature of v_1 when bulb is at $t°$.
t'_1 = estimated mean temperature of v_1 when bulb is at 0°.
t_2 = temperature of v_2 when bulb is at $t°$.
t'_2 = temperature of v_2 when bulb is at 0°.
a = expansion coefficient of nitrogen under constant volume.
β = linear coefficient of expansion of platinum-iridium alloy.

Writing $$A = \frac{v_1/V_0}{1+at'_1} + \frac{v_2/V_0}{1+at'_2}$$

and

$$B = \frac{v_1/V_0}{1+at_1} + \frac{v_2/V_0}{1+at_2}$$

the equation may be transformed into a more convenient form for computations:

$$1 + \alpha t = \frac{p}{p_0} \frac{1 + 3\beta t}{1 + \mathrm{A} - \frac{p}{p_0}\mathrm{B}}.$$

Here $3\beta t$ represents the correction for the expansion of the bulb and $\mathrm{A} - \frac{p}{p_0}\mathrm{B}$ is the correction for the unheated space. In computing p the mercury columns were corrected in the usual manner for temperature and latitude.

Gas Thermometer Measurements.—Table I contains some of the earlier results, which were obtained after the temperature gradient along the bulb had been partially corrected. During this series of observations, the temperature difference between the middle and either end of the bulb varied between 50 and 150 M.V. (5°· to 15°·). As it was impossible entirely to eliminate the gradient with the arrangement of coils in use at this time, the heating currents were adjusted so as to have the gradients toward the top and bottom of the bulb of opposite sign and of nearly equal value, thereby materially reducing the magnitude of the correction to be applied.

Before beginning this series of observations and again after its completion, the thermo-couple "P" was calibrated by determining its electromotive force at the zinc and copper melting points. From the results which follow it will be seen that the electromotive force of the thermoelement, at the temperature of melting copper, has been lowered 15 M.V. (1·2°) through iridium contamination during the series of measurements.

1906		Zinc.		Copper.	
April 28	F.*	3398		10488	
	M.	3398		10483	
			3398		10486
May 14	F.	3396		10469	
	M.	3398		10472	
			3397		10471

After these observations (Table I) the furnace was rebuilt. In place of the heating coil of platinum-iridium alloy, a coil of pure platinum was substituted. At the same time the arrangement of the two auxiliary heating coils was so modified that by proper adjustment of rheostats, the gradient along the bulb could be reduced to 0·5° or less.

In order to eliminate, as far as possible, any error due to the contamination of the thermo-couples with iridium, the couples

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* F = Freezing point, M = Melting point.

Table I.

Initial pressure, $302{\cdot}3^{\mathrm{mm}}$.
$a=0{\cdot}003665$.
Average temperature difference between middle and either end of bulb, 10°.
Equation used for "calculated" temperatures,

$$T = 50{\cdot}19 + 0{\cdot}11176E - 1{\cdot}289 \times 10^{-6}E^2.$$

1906	p_0 (mm)	Thermo-couple "P" Microvolts	Temperature Observed	Temperature Calculated	T (obs.)—T (cal.)
Apl. 30	30·209	3231·*	396·8°	397·8°	—1·0°
		4738·	550·4	550·8	— ·4
		6232·	696·5	696·6	— ·1
		7302·	797·6	797·5	+ ·1
		8428·	900·2	900·5	— ·3
		9547·	998·4	999·6	—1·2
		11004·	1123·5	1123·9	— ·4
May 1	30·220				
May 2		2961·*	368·6	369·8	—1·2
		4944·	571·2	571·2	— ·0
		6448·	717·8	717·2	+ ·6
		7525·	818·6	818·2	+ ·4
		8094·	869·7	870·3	— ·6
		9040·	954·5	955·1	— ·6
		9750·	1016·4	1017·3	— ·9
		10583·†	1089·9	1188·5	+1·4
May 3	30·229				
May 4		3928·	470·0	469·3	+ ·7
		5186·	595·2	595·1	+ ·2
		5944·	669·1	668·9	+ ·2
		6725·	743·8	743·4	+ ·4
		7755·	839·7	839·3	+ ·4
		9255·	973·1	974·1	—1·0
		10135·	1049·9	1050·4	— ·5
May 5	30·230				
May 7		3918·	468·0	468·3	— ·3
		6926·	762·8	762·4	+ ·4
		8910·	943·4	943·6	— ·2
		10631·	1092·8	1092·6	+ ·2
		11264·	1147·0	1145·4	+1·6
May 9	30·252				

were calibrated from time to time by metal melting point determinations. Columns 7 to 10 of Table II contain the

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* Observations below 415° were not used in computing the parabola.
† Temperature fell 2° during observation.

E.M.F's of the standard thermo-couple "W" for these calibrations.

As a check against accidental errors of observation, all observations were made in pairs, with an interval of from five

FIG. 8.

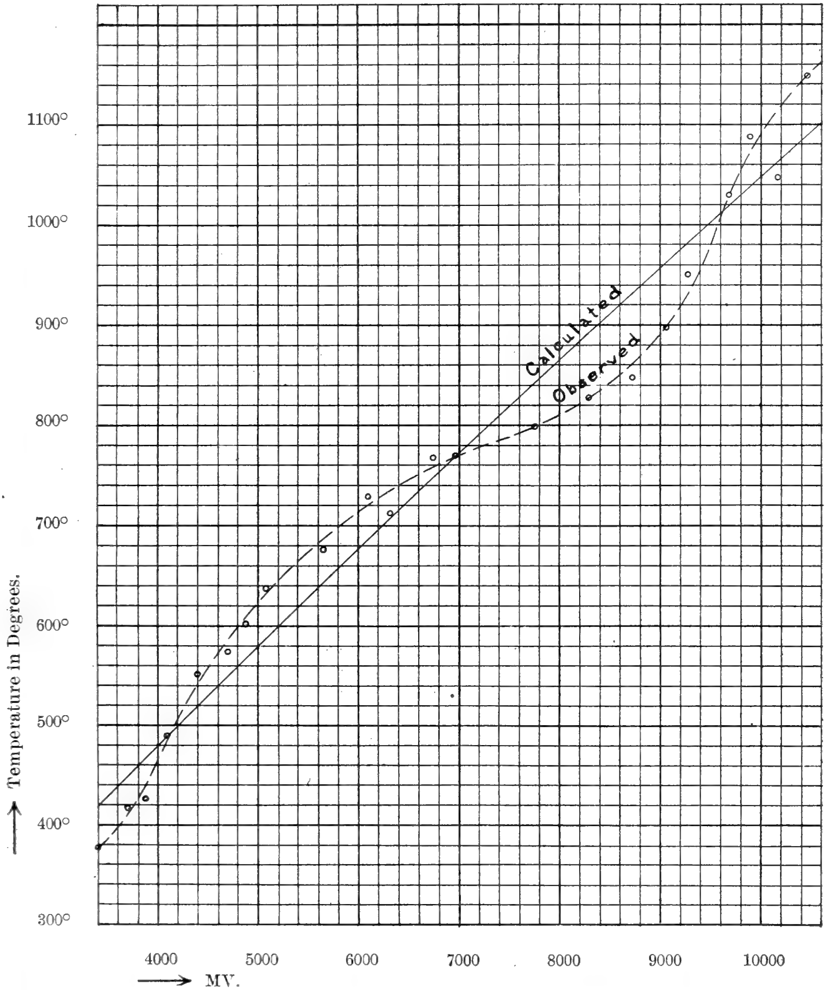

FIG. 8. Curves showing the systematic differences (much magnified) between the observations and the parabola which best represents them.
For the dotted curve the ordinate (above and below the full curve) is 1 div. = 0·2°.

to ten minutes between. The constants of the equation:

$$T = 51{\cdot}72 + 0{\cdot}112499E - 1{\cdot}35512 \times 10^{-6}E$$

TABLE II.

Thermo-couple "W." Initial pressure, $287{\cdot}5^{\text{mm}}$. $a=0{\cdot}003665$. Maximum temperature difference between middle and either end of bulb, 0·5°. Equation used for "calculated" temperatures,

$$T = 51{\cdot}72 + 0{\cdot}112499E - 1{\cdot}35512 \times 10^{-6} E^2$$

No.	Date	Initial Pressure P_0.	Thermo-couple "W" M.V.	Observed Temperature †	T (obs) — T (cal)	E.M.F. THERMO-COUPLE "W" Zinc	Silver	Gold	Copper
	1907								
	Feb. 4					3403			
	Mch. 6	28·755							
1	" 6		3367·	414·49°	— 0·64°				
2	" 6		3371·	414·96	— ·59				
3	" 6		3532·*	431·76	— ·40				
4	" 6		3536·*	432·25	— ·32				
	" 6	28·739							
5	" 7		3416·	419·96	— ·25				
6	" 7		3417·	420·00	— ·31				
7	" 7		3571·*	436·23	+ ·06				
8	" 7		3574·*	436·40	— ·08				
9	" 7		3789·*	458·55	+ ·03				
10	" 7		3793·*	458·94	+ ·01				
	" 9	28·734							
11	" 12		3309·*	408·51	— ·63				
12	" 12		3310·*	408·71	— ·53				
13	" 12		3430·	421·50	— ·15				
14	" 12		3429·	421·50	— ·04				
15	" 12		3540·*	432·83	— ·15				
16	" 12		3540·*	432·89	— ·09				
	" 13	28·735							
	" 14					F. 3405			10461.
						M. 3404			10461.
	" 14	28·735							
17	" 15		10430·5	1078·02	+ ·31				
18	" 15		10419·	1077·05	+ ·31				
	" 15	28·739							
	" 16								10463.
									10462.
19	" 20		9671·	1013·17	+ ·22				
20	" 20		9664·	1012·43	+ ·08				
21	" 20		10446·	1079·96	+ ·95				
22	" 20		10426·	1078·26	+ ·93				
23	" 20		10434·	1079·02	+ 1·02				
24	" 20		9895·5	1032·75	+ ·49				
25	" 20		9895·	1032·70	+ ·48				
	" 21/22					F. 3405			10457.
						M. 3405			10456.
	" 23	28·755							
	Apr. 2/3						F. 9046	10214	10454.
							F. 9046	10214	10454.
	" 22	28·751							
26	" 23		3383·	416·14	— ·70				
27	" 23		3384·	416·26	— ·64				
28	" 23		4393·	520·07	+ ·29				
29	" 23		4388·	519·71	+ ·44				
30	" 24		4095·	489·79	+ ·11				
31	" 24		4097·	489·89	+ ·01				

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* In computing the constants of Equation (1) the observations marked * in Table II were omitted in order to equalize the intervals between points.

† The column of "calculated" values has been omitted from Table II for the convenience of the printer. The column of observed temperatures and the column of differences together contain all the information required to reproduce the calculated values obtained from the equation above.

No.	Date		Initial Pressure P_0.	Thermo-couple “W” M. V.	Observed Temper-ature †	T (obs) − T (cal)	E.M.F. Thermo-couple “W”			
							Zinc	Silver	Gold	Copper
32	Apr.	24		5073·5	588·00°	+ ·40°				
33	“	24		5072·5	587·97	+ ·47				
34	“	24		6104·	688·44	+ ·52				
35	“	24	28·756	6099·5	687·84	+ ·35				
	“	25								
36	“	26		4700·5	550·81	+ ·23				
37	“	26		4698·	550·65	+ ·32				
38	“	26		6962·	769·49	+ ·23				
39	“	26		6957·5	768·86	+ ·03				
40	“	26		8020·5	866·45	− ·40				
41	“	26		8029·	867·99	+ ·37				
42	“	27		5648·	644·34	+ ·44				
43	“	27		5646·	644·24	+ ·55				
44	“	27		9036·	957·20	− ·42				
45	“	27		9054·	958·81	− ·39				
46	“	29		3718·	451·00	− ·26				
47	“	29		3716·	450·76	− ·29				
48	“	29		10190·5	1057·32	− ·10				
49	“	29	28·755	10188·	1057·09	− ·11				
	“	29								
	May	1/10					F. 3400	9046		
							M. 3400	9050		
50	“	13		3430·	421·19	− ·46				
51	“	13		3438·5	422·06	− ·47				
52	“	13		6771·5	751·52	+ ·15				
53	“	13		6769·5	751·36	+ ·18				
54	“	14		5845·5	663·62	+ ·59				
55	“	14		5848·	663·33	+ ·06				
56	“	14		9274·	978·10	− ·39				
57	“	14		9281·	978·82	− ·28				
58	“	16		4907·	571·49	+ ·37				
59	“	16		4906·	571·37	+ ·35				
60	“	16		7242·	795·42	+ ·05				
61	“	16		7243·	795·46	0				
62	“	16		7240·	795·24	+ ·06				
63	“	16		10188·	1056·91	− ·29				
64	“	16		10177·	1056·15	− ·12				
65	“	17		6338·	710·27	− ·03				
66	“	17		6341·	710·70	+ ·11				
67	“	17		8272·	888·96	− ·63				
68	“	17		8277·	889·50	− ·54				
69	“	17		9024·	955·74	− ·82				
70	“	17		9015·	955·01	− ·76				
71	“	18		3891·	468·56	− ·38				
72	“	18		3894·5	468·94	− ·35				
73	“	18		7730·	839·95	− ·41				
74	“	18		7725·	839·46	− ·45				
75	“	18		8741·	930·70	− ·84				
76	“	18		8740·	930·62	− ·83				
	“	19	28·763							
	“	20/22					F. 3398	9040	10212	
							M. 3398	9040	10216	
	“	23						F. 9042		
								M. 9042		

were computed by the method of least squares. In computing these constants the observations marked* in Table II were omitted in order to equalize the intervals between points. By comparing the T(obs.) − T (calcul.) values (Table II, column 6) of the various pairs of observations, it will be seen that any two values at the same temperature agree within 0·1°. With one exception, the differences between observed and calculated temperatures are all less than 1°. The average difference is 0·37° and the probable error of a single observation is 0·25°.

The foregoing table (Table II) contains a complete series of 76 observations, without omission, covering a period of more than three months in time, in the order in which they were made and with the control melting points through which the constancy of the thermoelements was assured. If we now regroup these observations in the order of increasing temperatures and combine the pairs referred to above, the relation between the observed and calculated curves appears in a new and interesting light. (Table III.) The average difference in column 5, Table III, is somewhat smaller than in Table II. The most notable feature, however, of these differences is their sytematic variation. Below 500° the observed values are less than the calculated ones; from 500° to 800° the observed values are greater, from 800° to 1000° the calculated values are greater and above 1000° the observed values are greater. If the calculated temperatures be taken as the ordinates of a curve of which the E.M.F's of element "W" are abscissas, the resulting curve will be a parabola, slightly concaved downward (fig. 8).

If now the differences in column 5, Table III, be plotted on their proper ordinates, measuring upward from this parabola when the difference is positive and downward when it is negative, the second curve will cross the first in three points, forming two loops of about equal length and area. In fig. 8 the dotted curve represents the observed temperature curve, with the deviation from the parabola plotted on an exaggerated scale. From this diagram, as well as from the figures in column 5 of Table III, it is apparent that a simple equation of the second degree is no longer quite competent to express the electromotive force of the thermo-couple as a function of temperature with the full accuracy of the measurement. In their paper on the electromotive force of metals of the platinum group, Holborn and Day† state that the "relation between the thermoelectric force and the temperature in metals of the platinum group could be represented, within wide limits, with an accuracy of ±1·0° by a function of the second degree." The results of our experiments are represented by a function

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† This Journal (4), viii, 46, 1899.

of the second degree, between 400° to 1100°, with an accuracy of ±0·5°. The differences between our observed temperatures and the temperatures calculated from formula I, however, cannot be attributed wholly to observational error on account of their systematic variation. For greater accuracy than 0·5° it will therefore be necessary to use a different equation—perhaps an equation of four parameters.

TABLE III.

$$(I)\ T = 51{\cdot}72 + 0{\cdot}112499E - 1{\cdot}35512 \times 10^{-6}E^2$$

No. of Observation	Thermo-couple "W" M. V.	Temperature Observed	Temperature Calculated	T (obs.)—T (cal.)
1, 2, 5, 6, 13, 14, 26, 27, 50, 51	3407·7	418·97	419·35	− ·38°
46, 47	3717·	450·88	451·16	− ·28
71, 72	3892·8	468·75	469·13	− ·38
30, 31	4096·	489·84	489·80	+ ·04
28, 29	4390·5	519·89	519·53	+ ·36
36, 37	4699·3	550·73	550·47	+ ·26
58, 59	4906·5	571·43	571·08	+ ·35
32, 33	5073·	587·99	587·56	+ ·43
42, 43	5647·	644·31	643·80	+ ·51
54, 55	5846·8	663·48	663·16	+ ·32
34, 35	6101·8	688·14	687·73	+ ·41
65, 66	6339·5	710·49	710·45	+ ·04
52, 53	6770·5	751·44	751·24	+ ·15
38, 39	6959·8	769·18	769·06	+ ·12
60, 61, 62	7241·7	795·37	795·35	+ ·02
73, 74	7727·5	839·71	840·15	− ·44
40, 41	8024·8	867·22	867·25	− ·03
67, 68	8274·5	889·23	889·82	− ·59
75, 76	8740·5	930·66	931·50	− ·84
44, 45, 69, 70	9032·2	956·68	957·28	− ·60
56, 57	9277·5	978·46	978·78	− ·32
19, 20	9667·5	1012·80	1012·67	+ ·13
24, 25	9895·3	1032·73	1032·25	+ ·48
48, 49, 63, 64	10185·9	1056·87	1057·04	− ·17
17, 18, 21, 22, 23	10430·0	1078·31	1077·68	+ ·63

The numbers in column 1, Table III, correspond to those in column 1, Table II. The figures in columns 2 and 3 represent the means of the corresponding figures of Table II indicated by the numbers.

After the series of observations represented by Tables II and III, the bulb was evacuated and refilled with nitrogen under a somewhat higher initial pressure, $p_0 = 325^{\mathrm{mm}}$. With this filling, the results contained in Table IV were obtained.

Table IV.

Thermo-couple "W."
Initial pressure 325^{mm}.
$a = \cdot003665$.
Equation used for calculated temperatures same as in Tables II and III.

$$T = 51{\cdot}72 + 0{\cdot}112499E - 1{\cdot}35512 \times 10^{-6}E^2.$$

1907	Thermo-couple "W" Microvolts	Temperature Observed	Temperature Calculated	T (obs.)—T (cal.)
June 3	4025·	482·10°	482·58°	— ·48°
	4026·	482·15	482·68	— ·53
	5009·	581·29	581·23	+ ·06
	5017·5	582·22	582·07	+ ·15
	5978·	675·32	675·81	— ·49
	5974·	675·07	675·43	— ·36
June 4	6238·5	700·88	700·81	+ ·07
	6239·	701·05	700·86	+ ·19
June 6	6992·	772·10	772·07	+ ·03
	6988·	771·72	771·70	+ ·02
May 29	7486·5	818·65	818·00	+ ·65
	7495·	819·00	818·78	+ ·22
June 4	7954·	860·52	860·81	— ·29
	7952·	860·47	860·63	— ·16
June 5	8488·5	908·47	909·03	— ·56
	8488·5	908·57	909·03	— ·46
June 4	9016·	955·30	955·86	— ·56
	9011·	954·91	955·42	— ·51
June 5	9474·	995·32	995·91	— ·59
	9480·	995·86	996·43	— ·57
June 6	9975·	1038·82	1039·07	— ·25
	9940·	1035·65	1035·22	+ ·43
	10197·5	1058·50	1058·53	— ·03

Column 5, Table IV, contains the differences between the observed temperatures and the temperatures calculated with the equation used in the previous series (Table III)

$$T = 51{\cdot}720 + {\cdot}11250E - 1{\cdot}35512 \times 10^{-6}E^2.$$

The average difference is 0·33°, and the maximum difference 0·65°.

The agreement between this series of observations and the preceding one is so extraordinarily close that not only the same equation serves for both but the differences "obs.–calc."

are of the *same order of magnitude and similarly distributed*, thereby confirming the conclusion that the observations are more accurate and consistent, within this temperature region, than the interpreting parabola.

Metallic Melting Points.—By way of establishing permanent records of these observations, the usual procedure was adopted of determining various metallic melting points which occur within the range of the temperatures investigated, with the thermoelements which had been directly compared with the gas thermometer. The metals chosen for this purpose were gold, silver, copper and zinc. Metal melting points were given the preference over pure salts which have been repeatedly suggested for this purpose, (1) on account of the greater sharpness of the melting point, (2) on account of their general availability for such determinations, and (3) because of the now very generally established custom of comparing the results of different observers through the medium of these standard melting points.

In choosing the materials for such determinations, two not altogether concordant standpoints must be recognized; (1) the materials used must be of absolutely known composition and of high purity in order to give the melting point determinations a positive significance; (2) the same materials in the same purity must be easily obtainable by other investigators in order to enable the results to be conveniently utilized by others if desired. The metals used in this investigation were from various sources which will be specified below. Each has been very carefully described and analyzed by Dr. E. T. Allen of this laboratory, whose report is printed in full. We prepared none of the metals ourselves. Those which were used were purchased from firms who may fairly be expected to supply the same nominal quality to any other investigator who may care to use them, but it must be emphasized in this connection that metals furnished under the same description by the same dealer at different times have not always proved of uniform purity and probably cannot at present be expected to do so. The variations in the thermal behavior of the different samples is not great, never amounting to more than 1° in our experience; but we are of course unable to offer any guarantee that the same metals obtained in future will remain within this limit, nor is the dealer's guarantee at present a sufficient protection.

As the situation now stands, the errors in the gas thermometer measurements are rather smaller than the differences between the melting points of different samples of a given metal obtained at different times from the same dealer and of the same (nominal) purity. This may serve to emphasize more than ever before the desirability of some provision, preferably by the Bureau of Standards, for standard metals, the uniform purity of which can be absolutely depended upon, in terms of which such constants can be expressed. In the absence of such a provision, it is difficult to see just how to make the gas scale conveniently available for general use in its full accuracy. This is furthermore a matter of considerable importance in view of the extended extrapolation to which the gas scale is frequently subjected by the use of thermoelements or otherwise. Supposing the metal melting points to be capable of reproducing the temperature curve correct within 1° at the copper point (1081°), the extrapolation to 1500° may easily remain uncertain by at least 5° in the hands of different individuals using the same functions for the extrapolation.

Nor is this the only difficulty to which this use of standard melting points may lead. On account of the systematic errors attending the application of an equation of the second degree to the gas thermometer observations, to which reference has been made (p. 448), the usual standard melting points are not competent to reproduce the gas scale exactly. A curve of the second degree, developed by least square solution from seventy-six observations which show systematic deviation, cannot be reproduced with only the three observations which chance to represent the standard melting points. This will be immediately apparent, though on a somewhat exaggerated scale, if we locate on the *dotted* curve in fig. 8 the temperatures corresponding to the zinc (419·5°), silver (957·9°) and copper (1080·9°) points and then undertake to reproduce the "calculated" curve from them alone.

As this is the method almost universally used for the purpose, it is worth while indicating by a special case exactly where it leads. Column 3 of the table below contains the actual melting points of four of the purest metals interpolated from gas thermometer observations close by. Column 4 contains the same points computed from Equation I. If

Table V.

	Element "W"	Temperatures extrapolated from nearest observation	Temperatures Calculated I	Difference
Zinc	3403·	418·48	418·87	—·39
Silver	9046·	957·90	958·50	—·60
Gold	10214·	1059·26	1059·42	—·16
Copper	10461·	1080·92	1080·29	+·63

now, following the usual practice, we take the melting temperatures of zinc, silver and copper and pass a parabola through these, we obtain

$$T=55{\cdot}51+0{\cdot}110789\,E-1{\cdot}2197\,(10)^{-6}E^2 \quad \text{(Equation II)}$$

instead of Equation I. And if, by way of illustration, we recompute all the temperatures of Table III, using this new equation and compare the results with those obtained from Equation I, we have an illustration (Table VI) of the effect of

TABLE VI.

Equation I $T=51{\cdot}72+0{\cdot}112499\,E-1{\cdot}35512\,(10)^{-6}E^2$

Equation II $T=55{\cdot}51+0{\cdot}110789\,E-1{\cdot}2197\,(10)^{-6}E^2$

No. of Observation	Temperature Observed	Temperature Calculated I	Temperature Calculated II	Obs.-Calc. I	Obs-Calc. II
1, 2, 5, 6, 13, 14 26, 27, 50, 51	418·97°	419·35°	418·97°	—·38°	0·00
46, 47	450·88	451·16	450·46	—·28	+0·42
71, 72	468·75	469·13	468·31	—·38	+0·44
30, 31	489·84	489·80	488·84	+·04	+1·00
28, 29	519·89	519·53	518·42	+·36	+1·47
36, 37	550·73	550·47	549·21	+·26	+1·52
58, 59	571·43	571·08	569·73	+·35	+1·70
32, 33	587·99	587·56	586·15	+·43	+1·84
42, 43	644·31	643·80	642·24	+·51	+2·07
54, 55	663·48	663·16	661·58	+·32	+1·90
34, 35	688·14	687·73	686·11	+·41	+2·03
65, 66	710·49	710·45	708.84	+·04	+1·65
52, 53	751·44	751·24	749·70	+·15	+1·74
38, 39	769·18	769·06	767·50	+·12	+1·68
60, 61, 62	795·37	795·35	793·85	+·02	+1·52
73, 74	839·71	840·15	838·80	—·44	+0·91
40, 41	867·22	867·25	866·04	—·03	+1·18
67, 68	889·23	889·82	888·72	—·59	+0·51
75, 76	930·66	931·50	930·68	—·84	—0·02
44, 45, 69, 70	956·68	957·28	956·68	—·60	0·00
56, 57	978·46	978·78	978·35	—·32	+0·11
19, 20	1012·80	1012·67	1012·57	+·13	+0·23
24, 25	1032·73	1032·25	1032·37	+·48	+0·36
48, 49, 63, 64	1056·87	1057·04	1057·45	—·17	—0·58
17,18,21,22,23	1078·31	1077·68	1078·31°	+·63	0·00

interpolation of this character even when used with the best experimental data which we have obtained. The error amounts to 2° in the region 600–700°.

The solution of this difficulty is obviously to obtain additional fixed points and thereby to reduce the interval for interpolation but we have so far found difficulty in obtaining suitable substances. The metals which melt in the desired region either are not obtainable in uniform purity or easily become oxidized or otherwise contaminated during the manipulation necessary for a melting point determination. Suitable eutectic mixtures may eventually offer a solution of the difficulty.

*The Metals Used.**—After some investigation, it was found that we could obtain in sufficient quantity, silver, copper and zinc which ranged in purity from about 99·94 per cent to 99·997 per cent, and gold which was probably still purer. These figures do not include oxygen nor carbon (except in case of the silver), for, since the melting points of the metals had to be determined in carbon crucibles, it is evident that the presence of these impurities would have no significance for present purposes. Of course it would have been possible to prepare these metals, or at least the zinc and copper, in still purer condition, but it was not thought to be worth while, since it is improbable that the most refined of present-day methods could safely determine any difference between the melting points of the chemically pure metals and those actually used.

The Gold.—About 250 grams of "proof gold" were obtained from the Philadelphia Mint. It was prepared by Mr. Jacob Eckfeldt. A sample of gold prepared in a similar manner by Mr. Eckfeldt was used by Prof. Mallet in his determination of the atomic weight of this metal. The method of purification is given in the Am. Chem. Jour., vii, 73, 1889. Prof. Mallet found no systematic difference between this gold and two other samples, one of which was obtained from the Mint of England, and the other of which was prepared by himself. In view of these facts, it was evidently unnecessary to analyze the gold.

Regarding the methods which were used in the analysis of the silver, copper and zinc, there will be no need of giving all the details, especially where accurate methods of procedure are well known, but in view of the very small quantity of impurities estimated, some explanation and some conclusions as to the accuracy of the data will be presented. Most of the work was done in a new laboratory under exceptionally favorable conditions of cleanliness; large samples, generally 100 grams, were taken for analysis and the reagents were subjected to rigid examination. Separations were always repeated, in

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* By E. T. Allen.

some cases many times, and filtrates were not rejected until they had been reduced to small volumes and had been proved free from the elements looked for. Of course, the accuracy of such work is most satisfactorily tested by synthetical methods. Mylius and Fromm,* by using a preparation of metallic zinc in which they could find no impurities, were able to detect *qualitatively* as little as $0{\cdot}1^{mg}$ of lead, cadmium or mercury, in a solution containing 40 grams of zinc, without difficulty. *Quantitatively*, I have never found greater variations than ·002 per cent in duplicate determinations of the heavy metals in silver, copper or zinc, with a single exception which was rejected, and some of the figures agree closely in the ten thousands of a per cent.

The Silver.—This metal as well as the gold, was prepared by Mr. Eckfeldt at the Philadelphia Mint. A block weighing about 100 grams was cut from a larger brick with a hard cold chisel, and after cleaning, transferred to a large casserole of Berlin porcelain and dissolved in a slight excess of nitric acid. During the operation the dish was covered with a watch glass. A small black residue was now filtered off on the felt of a large porcelain Gooch crucible, washed and dried. The asbestos of the felt was previously heated to redness. The residue was then laid in a porcelain boat which was slipped into a combustion tube containing copper oxide and heated in a current of oxygen. The outflowing gas was passed through a very dilute standard solution of barium hydroxide, $1^{cc} = 0{\cdot}97^{mg}$ of CO_2, in which a decided white precipitate appeared at once. The excess of baryta was then titrated with standard acid. A blank determination *previously* made gave no precipitate in the baryta water. This determination is of no importance as regards the melting point of the silver, since the metal had to be melted in graphite, but considering the source of the silver and its unusual degree of purity, the determination may be of some interest. What remained of the residue after the carbon was burned, was extracted with aqua regia. The solution was evaporated to dryness, taken up with hydrochloric acid and the gold precipitated by sulphur dioxide. The filtrate from gold gave a slight black precipitate with hydrogen sulphide. This precipitate weighed only $0{\cdot}1^{mg}$ after it had been glowed in a small porcelain crucible, but it remained black, dissolved in a few drops of aqua regia which left a yellow stain when evaporated, and gave a very strong rose color when dissolved in water and tested with a drop of potassium iodide,—all characteristic of platinum. It was suspected that a trace of platinum might exist in the acid used to dissolve the silver, but a blank test on the same quantity of

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* Zeitschr. anorg. Chem., ix, 144, 1895.

reagent proved the contrary. The silver solution was now diluted to several liters and precipitated with hydrochloric acid. The filtrate was evaporated in porcelain to a small volume and in this the remaining impurities were sought for by well-known methods. Only lead and iron and the merest trace of copper were found. A blank determination was made for iron. Found in the silver + reagents, ·0013 per cent; in the reagents, ·0002 per cent; leaving ·0011 per cent in the silver.

For the estimation of sulphur, a separate portion of 38 grams was taken, the silver was removed in the same manner, and the filtrate evaporated to dryness in porcelain. The small residue was then evaporated again with hydrochloric acid to decompose nitrates. The final residue was dissolved in a small volume of water acidulated with hydrochloric acid, filtered to remove any silver chloride which might have escaped precipitation and precipitated with barium chloride. Found 1·4^{mg} $BaSO_4$, while the same quantity of reagents gave 0·4^{mg} $BaSO_4$: S = ·0004 per cent.

Analysis of Silver.

As	none
Sb	"
Sr	"
Au	·0005
Pt	·0001
Cu	merest trace
Bi	none
Pb	·0008
Hg	none
Cd	"
Zn	"
Ni	"
Co	"
Fe	·0011
S	·0004
C	·0003
	·0032 %

The Copper.—The copper was of the form known as "copper drops cooled in hydrogen" and was obtained from Eimer and Amend of New York. Not all copper of this brand is equally pure. The sample analyzed was a portion of a 25 lb. lot. The method followed in the analysis was essentially that of Hampe,* in which the copper is separated from the impurities by precipitation as cuprous thiocyanate. A 100-gram por-

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*Lunge, Chem.-tech. Methoden, ii, 202. Chem. Ztg. 1691, 1893.

tion was placed in a large casserole of Berlin porcelain, dissolved in nitric and sulphuric acids and the solution then evaporated to drive off the excess of nitric acid. This troublesome operation can be greatly facilitated by the use of a crown burner, though as dilution and evaporation have to be several times repeated, small losses are difficult to prevent. Duplicate determinations, however, proved that they were entirely negligible as regards the small percentage of impurities. The sulphate of copper was now dissolved in water and diluted. A little HCl was added, and after standing, the solution was filtered. The residue left on the filter was extracted with ammonia to remove silver chloride and the remaining part of it was treated with aqua regia. There was still left a little silica, from the porcelain dish in which the copper was dissolved. The solution obtained by aqua regia after the nitric acid was entirely driven out by hydrochloric acid, was tested for gold by sulphur dioxide. There was no precipitate in the cold even after long standing, though evaporation caused the precipitation of about half a milligram of black metal. This remained black on heating, dissolved only partially and with difficulty in aqua regia, and with sulphuric acid and ammonium nitrate gave a faint blue color. These tests indicate iridium, though there was too little to identify with certainty. The rest of the solution which had been tested for gold was precipitated by hydrogen sulphide and the precipitate was filtered, washed and burned in a porcelain capsule. It formed a yellow chloride with aqua regia, gave a precipitate with ammonium chloride and a very strong test for platinum with potassium iodide. This platinum did not come from the acids used to dissolve the copper, since the same quantities were very carefully tested by hydrogen sulphide after nearly the whole portion had been driven off by heating in porcelain, and found to contain not a trace.

The solution containing the copper was then warmed and saturated with sulphur dioxide. After standing, a further portion of silver was precipitated, filtered off and washed. It was then dissolved in a little nitric acid, precipitated again as chloride and added to the main portion of the silver chloride, which was dried at 130° and weighed.

The solution still containing the copper was diluted to about 8 liters, and from it all but a small portion of the copper was precipitated by a standard solution of potassium thiocyanate, 1^{cc} of which was equivalent to about 50^{mg} of copper. The thiocyanate was proved to be free from heavy metals by a test with hydrogen sulphide. The small amount of iron which it contained was separated before the solution was standardized, by the addition of a little ammonium alum followed by ammonia. The solution was allowed to stand and then filtered from iron and alumina. The precipitation of the copper was done very gradually with constant shaking to avoid carrying down the impurities, and after long standing was filtered. The filtrate was concentrated to a small volume in porcelain. A small additional precipitate which came down in this process was worked over with care to avoid any possible loss of impurities, especially lead, though no metal but copper was found in it. The filtrate was then examined as usual. A word is needed in reference to the presence of zinc. This was found in every sample examined, in fact, it was generally the chief impurity. It was suggested that this zinc or at least a part of it might have come from the large flasks of Jena glass in which the acid solutions of the copper stood. To test this point, a sample of copper in which had been found ·089 per cent of zinc was tested again. In this determination Jena glass was entirely discarded. The zinc found was ·091 per cent. As these results agree within the limits of error, it is evident that Jena glass under these conditions will not contaminate solutions with zinc, at least in quantities of this order of magnitude. For the determination of silicon in the copper, 25 grams were placed in a platinum basin, dissolved in nitric and sulphur acids, and evaporated over a crown burner to white fumes. The residue was dissolved and filtered. The filter was burned and the small residue tested for silica by hydrofluoric and sulphuric acids. Since it was feared that some silica might come from the watch glass used to cover the platinum dish during this operation, a blank was carried out with the reagents under the same conditions. Within the limits of error none was found.

For the estimation of sulphur the method of Lobry de Bruyn* was used, in which the copper is separated from the nitric acid solution by electrolysis. Twenty-five grams of metal was dissolved in 75^{cc} nitric acid diluted with about an equal quantity of water, and then the excess of acid evaporated as far as possible on the steam bath. The electrolysis was done in a large platinum basin, which served as a cathode. The basin was covered with a glass plate pierced to admit a cylindrical platinum crucible which formed the anode. The current density was about $\cdot 015 \frac{\text{amp.}}{\text{sq. cm.}}$ After a time it was found necessary to pour off the solution from the precipitated copper and remove the free acid by another evaporation. A repetition of this operation is advisable. The filtrate from the copper is evaporated to dryness in porcelain and the small residue of nitrates decomposed by hydrochloric acid. The final residue

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* R. des trav. Chim. de Pays Bas, x, 125, 1891.

is dissolved in acidulated water and precipitated by barium chloride.

Found in 25 grams copper, $4{\cdot}2^{\text{mg}}$ $BaSO_4$
" " 75^{cc} nitric acid, 0·6 " "
$3{\cdot}6^{\text{mg}}$ $BaSO_4$ = ·002 per cent.

Analysis of Copper.

As	none
Sb	"
Sn	"
Se	"
Te	"
Au	"
Pt metals	·0011
Ag	·0007 and ·0005*
Bi	none
Pb	"
Cd	"
Zn	·0007
Ni	none
Co	"
Fe	·0038
Si	none
S	·0020
	·0083

The Zinc.—This metal was obtained in the form of sticks from the firm of Eimer and Amend. The method of Mylius and Fromm was followed for the principal impurities.† 100 grams were dissolved in nitric acid. The solution was then diluted and ammonia was added until the zinc at first precipitated was entirely redissolved. Then enough hydrogen sulphide was added to throw down all the impurities of the hydrogen sulphide and ammonium sulphide groups together with considerable zinc. The precipitate was filtered off and further separations were made as usual.

The platinum metals and gold were not looked for as it was thought quite improbable they would be present, but arsenic and antimony were sought for by Günther's method.‡ This consists in the volatilization of the hydrides of these metals which are separated from the hydrogen which forms at the same time by passing the gas through silver nitrate solution. A special form of apparatus was used which consists of a 1 liter round-bottom flask with long neck 35^{mm} wide at the top.

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* Two separate determinations.

† Zeitschr. anorg. Chem., ix, 149, 1895.

‡ Lunge, Chem.-tech. Methoden, ii, 322. Zeistchr. analyst. Chem., xx, 503.

This is closed by a glass stopper in which are sealed a small glass tube passing to the bottom of the flask and serving to fill the flask with hydrogen and to replace the gases formed in the experiment; a dropping funnel through which the acid used to dissolve the zinc is introduced, and lastly, an upright outlet tube surrounded by a small condenser. The outlet was connected with a wash bottle containing a solution of silver nitrate. As pure zinc dissolves with difficulty in dilute hydrochloric acid, the metal was reduced to the form of shavings by the aid of a lathe. Fifty grams of these shavings were introduced into the flask, the air in which was at once replaced by hydrogen. Dilute hydrochloric acid was then let in through the dropping funnel. The solution was facilitated by warming. At the end of the operation, the gas in the flask was driven out by pure hydrogen. The silver nitrate solution which contained a black precipitate was then filtered. The antimony in the precipitate was determined by dissolving it in nitric acid with the addition of a little tartaric acid, precipitating the silver with hydrochloric acid, evaporating the filtrate to dryness on the steam bath and precipitating by hydrogen sulphide. The precipitate was dissolved in a few drops of ammonium sulphide, the solution filtered into a small tared porcelain capsule, evaporated, decomposed by nitric acid and weighed as Sb_2O_4. After separating the silver from the first filtrate which contained the arsenic, it was evaporated to dryness, reduced with sulphurous acid and precipitated by hydrogen sulphide. None was detected with certainty.

Analysis of Zinc.

As	None found
Sb	·002
Sn	Not looked for
Au	"
Pt	"
Ag	None
Bi	"
Pb	·051
Cd	·004
Ni	None
Co	"
Fe	·006
Si	None
S	"
	·063

If this solution had been tested by Marsh's method, no doubt a trace would have been found, but as its quantity was of a different order of magnitude from the other impurities it was not thought worth while to make the test. Günther determines sulphur at the same time with arsenic and antimony, by interposing between the generator and the absorption cylinder which contains the silver nitrate another cylinder containing potassium-cadmium cyanide which absorbs all the hydrogen sulphide and according to him retains no arsenic and antimony. Since a solution of this cadmium compound is always alkaline, it was thought safer to take a separate portion of zinc for the estimation of sulphur, silver nitrate being used as the absorption reagent. The small precipitate was examined for sulphur by dissolving in nitric acid and proceeding as usual. Found 0·4^{mg} $BaSO_4$. Blank gave 0·3^{mg} $BaSO_4$.

The zinc was tested for silicon in the same way as the copper.

Redeterminations with other metal samples.—The zinc, silver and copper melting points were redetermined in 1908 with other metal samples from the same sources as before and serve to show the accuracy which may be expected in random samples of the same (nominal) purity. The gold was not redetermined for the reason that no second charge was available, nor indeed was a redetermination deemed necessary.* Complete analyses of these samples have not been made, but such tests as were undertaken serve to show that the copper was even purer than that of which the analysis is given. The results of these determinations are shown in the following table: †

1908	Metal	Thermo-Couple "W" Micro-volts	Temperature
March 10	Zinc	3404·	418·58
March 12	Silver in CO	9055·	958·78
April 10	Copper in CO	10476·	1081·5

Following are the most probable values of the metal melting points:

Zinc	418·5° ± 0·1°
Silver	958·3 ± 0·5
Gold	1059·3 ± 1·0
Copper	1081·0 ± 0·5

Summary.

The gas thermometer problem at the present stage of its development has become primarily a problem for experimental study with two definite purposes, one to increase the accuracy

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* Sometime after our work with gold had been completed a reëxamination of the charcoal which had been used to cover the surface of the metal during melting, very unexpectedly yielded iron. The gold was also found slightly contaminated with iron. The gold point here offered is, therefore, no longer entirely above suspicion and will now be repeated as soon as a fresh charge can be obtained. The probable error is accordingly given much larger than the original measurements indicated.

† Determinations by R. B. Sosman.

of the measurements, the other to increase their range. The application of the gas laws is no longer subject to serious question. The progress of recent years has given us electric heating in place of gas and the consequent possibility of controlling the temperature with great certainty and exactness. It has also given us the metal bulb with a definite and measurable expansion coefficient and capable of holding the expanding gas without loss. It has discovered a gas which does not diffuse through the bulb or react with it chemically, which does not dissociate within the limits of practicable measurement, and of which the expansion can be expressed with reasonable certainty in terms of the Kelvin thermodynamic scale. It has discovered the source of the errors in the thermoelements and a way to avoid them.

In 1904, Prof. Holborn of the Reichsanstalt increased the range of this scale as far as 1600° C., the probable error of the new portion being 10°. Simultaneously with this effort, work was begun at the Geophysical Laboratory in Washington with a view to increasing the accuracy of the scale, first over the existing range (to 1150°), and later, as much beyond this point as it should prove possible to go. Temperature measurements between 250° and 1150° have now been made and form the subject of the present paper. The particular points to which we have given the most attention are the following: (1) To provide a uniform temperature along the bulb by a suitable arrangement of the heating coils. (2) To enclose the furnace in a gas-tight bomb in which the pressure outside the bulb can be maintained equal to that within for all temperatures. This offers three distinct advantages: It provides against the deformation of the bulb through differences of pressure within and without in the region where the bulb material becomes softer. By using the same gas within and without, there is no tendency to diffuse through the bulb wall. It enables the initial pressure to be varied within considerable limits, thereby increasing both the scope and sensitiveness of the manometer. The sensitiveness in our instrument with this arrangement was about three times that of the Reichsanstalt. (3) The expansion of the bulb material was determined with great care and is probably accurate within 1/2 per cent. (4) The unheated space between the bulb and manometer has been reduced until the total correction in this hitherto uncertain region amounts to less than 5° at 1100°. An error of 5 per cent in the determination of its volume or temperature distribution is, therefore, practically negligible. It is probable that these changes serve to reduce the aggregate error of the gas thermometer in the region of 1100° to about one-tenth the magnitude which existed at the time of the establishment of the present scale.

Furthermore, and most important of all, these refinements are not limited to this temperature region. It is therefore reasonably probable that the gas scale can be extended to 1500° or 1600° with a proportionately small error in its absolute value. The immediate future of the present investigation will be to undertake this extension.

The interpretation of these measurements in terms of the melting points of readily available substances encounters certain difficulties. The melting point of pure salts is not sufficiently sharp and is somewhat difficult of interpretation. The metals which have commonly been used for the purpose are not obtainable commercially in sufficiently uniform purity to guarantee an accuracy within 1° at the higher temperatures. This is too large an error for the interpretation of the gas thermometer scale in its present refinement. No effort has been made to prepare metals in our own laboratory of exceptional purity for the reason that such metals would not be available for general use and would therefore be of little service.

We have accordingly adopted metals which are carried permanently in stock by dealers (whose names are given in connection with each) from whom the same metal in a nominal quality equal to that which we used can readily be obtained. We have analyzed these with extreme care to show the exact content of the sample supplied to us. We have duplicated the purchases ourselves, and have found no errors greater than 1° in their melting point determinations.

Another difficulty arises from the fact that the melting points of the purest metals available for use as constants in reproducing a high temperature scale (zinc, silver, gold and copper) are distributed in such a way that, although they may be *located* upon the gas thermometer scale with a probable error not greater than 0·5°, the calculation of a similar curve passing through these points does not suffice to *reproduce* the scale with this accuracy. In the region midway between zinc (418·9°) and silver (958·5°) the error of interpolation may amount to 2° even with metals of exceptional purity. Extrapolation is even more uncertain. This can be avoided by locating intermediate points which are equally trustworthy, if such can be found. We have not been fortunate enough to find points which fulfil these conditions satisfactorily but hope that we may yet be able to do so.

As the matter now stands therefore we have succeeded in perfecting the constant volume gas thermometer until the aggregate error affecting the measurements between 300° and 1150° appears not to be greater than 0·5°, but we are not yet able to offer adequate assurance that our scale can be reproduced by another with this accuracy. This matter will receive further attention in a later paper.

Geophysical Laboratory, Carnegie Institution
of Washington, August, 1908.

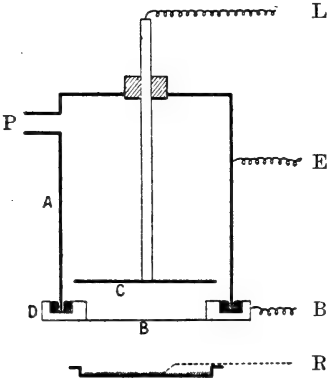
Art. XLIII.—*On the Range of the α-Rays*; by William Duane.*

The researches of Madame Curie, of Bragg and Kleeman, and of Rutherford have shown that the α-rays abruptly lose their powers of ionizing gases, of affecting a photographic plate, and of producing phosphorescence after they have penetrated several centimeters of air or an equivalent thickness of other substances. Further, Rutherford has found that near the point where it loses these powers the α-particle still possesses sixty per cent or more of its initial velocity.

Several years ago I made some experiments to determine whether the charge carried by the α-particle could be detected beyond the limit of its ionizing power, or, possibly, off to one side of its range. The results were negative. Recently I have taken up the research again at the laboratory of Madame Curie of the University of Paris, with more and purer radium, and with the additional purpose of investigating the power of the α-rays to produce secondary rays, and the transformation of the kinetic energy of the α-particles into heat.

Figure 1 represents the arrangement of the apparatus. A is a cylindrical box of brass $3{\cdot}8^{\mathrm{cm}}$ long and $3{\cdot}3^{\mathrm{cm}}$ in diameter. A round hole ($1{\cdot}8^{\mathrm{cm}}$ in diameter) in the bottom of the box is covered with a very thin sheet of mica, B. The mica weighs only 2 milligrams per square centimeter, and is reinforced on the inside by a grating of fine wires. It is so thin that the α-rays can pass through it easily, and strike the plate C, which is connected to an electroscope or electrometer and serves as an electrode. In order that a magnetic field may be produced parallel to the plate B and to the mica window, the apparatus is placed between the poles of an electromagnet; and in order to produce an electric field between the electrode and the window, the ring D, to which the mica is fastened, is insulated from the sides of the box by wax, and connected to the pole of a battery.

Fig. 1.



Connections: P, to pump; L, to electrometer or electroscope; E, to earth; B, to battery; R, radium.

The method of procedure follows: A very small quantity of radium chloride was dissolved in water and recrystallized twice

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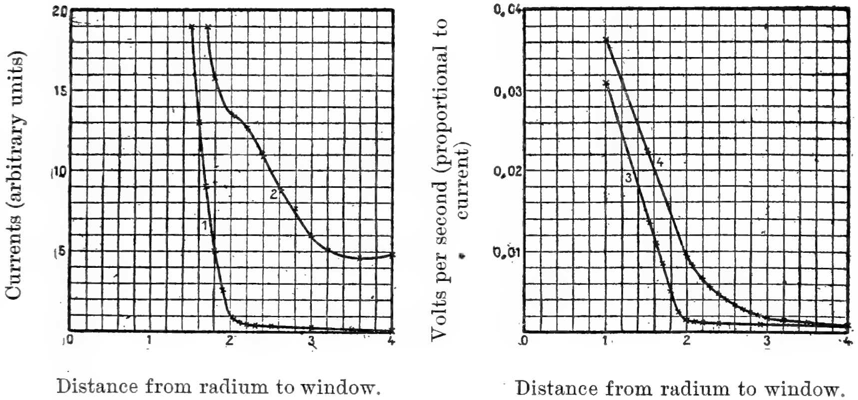
* Abstract of notes presented to the French Academy of Sciences. Comptes Rendus, 11th and 25th of May, 1908.

in succession at an interval of several hours, in order to free it from most of its emanation and induced activity. Finally it was dried upon a flat sheet of platinum. The platinum was then held horizontally below the mica window at different distances from it, and the ionization currents between the window and the electrode were measured by a quadrant electrometer, the window being at a potential of 88 volts above the electrode. To make the rays that entered the box parallel to each other a set of fine glass tubes (not shown in the figure) was fastened between the radium and the window with their axes vertical.

Curve 1, figure 2, represents the ionization current as a function of the distance from the radium to the bottom of the box. It is evident that *most of the ionization in the interior of the box disappears if the radium is removed to a distance from the window greater than about* 2$^{\mathrm{cm}}$.

Fig. 2.



The currents for distances greater than two centimeters are due to a small amount of emanation and induced activity remaining after or having accumulated since the final crystallization. The α-rays from these, as is well known, have greater ranges than have the α-rays from radium itself. The ionization due to these α-rays of longer range is well shown by curve 2, which represents the currents due to radium (a smaller amount than before) that had been left two days in a dry state, and which therefore contained considerable amounts of emanation and induced activity.

In order to measure the positive charge of electricity carried by the α-rays, I exhausted the air from the box by means of a mercury pump, producing a high vacuum of less than $\cdot 0001^{\mathrm{mm}}$

of mercury as measured by a McCleod gauge. This was to prevent the charge being neutralized by the ionization of the air in the box. I then measured the current flowing toward the electrode by means of a Wilson gold leaf electroscope, using much more radium than before (about 2 milligrams of pure radium chloride). For these measurements the set of fine glass tubes between the radium and the window was not used, and the window was kept at zero potential.

When the a-rays pass through the mica and when they strike the metal electrode they produce slow-moving secondary rays. In order to suppress these a magnetic field was produced parallel to the surfaces of the electrode and window. That the magnetic field stopped all the secondary rays was proved by the fact that increasing its strength from 2400 gauss to 3600 gauss did not alter the current flowing to the electrode.

That there was no appreciable ionization current in the interior of the box is shown by the fact that with the magnetic field a difference of potential of several volts between the window and the electrode did not alter the current from one to the other.

Curve 3, figure 2, represents the currents of electricity carried to the electrode by the a-rays. It is evident that *the greater part of the charge carried by the rays does not pass through the mica and reach the electrode, if the radium is more than* 2^{cm} *from the window.* This is the same critical distance as found before for the ionization. By reason of the form of the curves near the limit it is difficult to estimate the exact length of the range, but we can say that *approximately the charge of the a-particles and the ionization produced by them stop at the same point.*

Curve 4 represents the currents due to radium in which the emanation and induced activity had been allowed to accumulate for over two days. The currents for distances greater than 2^{cm} are due to the charges of electricity carried by the rays from the emanation, and radium A, and C.

In order to determine whether or not the a-rays lose their power of producing secondary rays at the point where the charge and ionization stop, the currents without the magnetic field were measured with the radium at different distances from the window. Under these conditions the current of electricity carried to the electrode is to some extent masked by the secondary rays produced at the lower surface of the electrode and the upper surface of the window. If a is the current carried to the electrode by the a-rays, s_1 the negative charge carried per second by the secondary rays away from the electrode, and s_2 the negative charge carried per second to the electrode by the secondary rays from the window, the total current toward the electrode is

$$i=a+s_1—s_2$$

The secondary rays s_1 and s_2 are stopped by the magnetic fields, leaving only the current *a*.

If the window is charged positively the electric field from it toward the electrode stops part (if strong enough all) of the current s_2, and if the window is charged negatively some or all of the current s_1 is stopped.

To determine how strong the field must be in order to stop all of the secondary rays, the radium was placed 1·5$^{\mathrm{cm}}$ below the window, and the currents toward the electrode measured by the Wilson electroscope when the window was charged to different positive potentials. The following values were obtained:

Potential	+ 0	2	4	9·5	17	25	34	51	68	85	170	volts.
Current	1·35	2·10	2·71	4·23	5·57	7·72	8·30	9·2	9·8	10·0	10·0	

It is evident from these figures that after a potential of some 70 volts is reached the current is not increased even if the potential is doubled: i. e., 70 volts stops all of the secondary rays coming from the window. If the field is reversed about the same potential, 70 volts stops all of the rays coming from the electrode.

The above readings were taken without a magnetic field. If a magnetic field of 2800 gauss is produced the current is 1·6 on the same scale, and is increased only a few per cent even by 170 volts.

We now have a means of studying the secondary rays coming from the surface of the electrode alone, s_1, for by charging the window to a potential of + 70 volts or more the current s_2 is suppressed. Then the difference between the currents with and without the magnetic field is s_1, the secondary rays from the electrode.

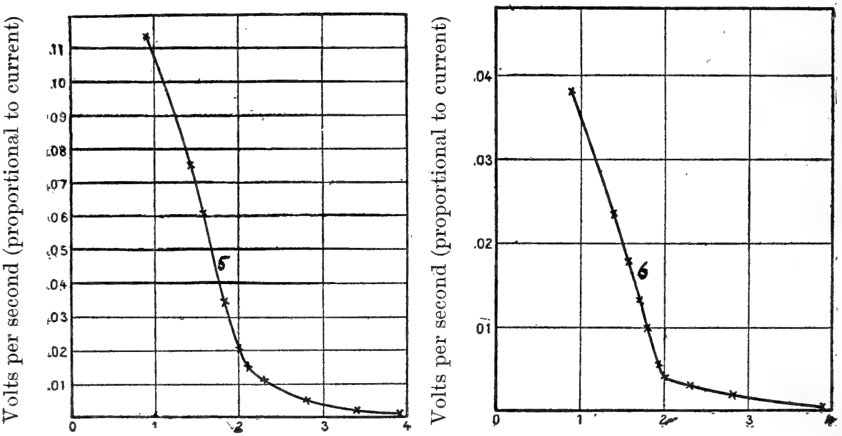
To determine whether or not the power of the *α*-rays to produce the secondary rays ceases at the point where the charge and the ionization stop, the 2$^{\mathrm{mg}}$ of radium chloride were freed from emanation and induced activity as before, and placed at different distances below the window. The window was charged to a potential of +85 volts, and the currents for each distance were measured, first without and then with, the magnetic field. The difference between the two currents, representing the secondary rays from the electrode cut off by the magnetic field, is represented in fig. 3, curve 5, as a function of the distance of the radium from the window.

It is evident that the greater portion of the *secondary rays stop when the radium is removed further than about* 2^{cm} *from the window;* and this is about the same distance as found before for the charge of *a*-rays and the ionization.

For better comparison the currents measured in the same series with the magnetic field, representing the charge carried by the *a*-rays, are plotted on curve 6, fig. 3.

Owing to the form of the curves it is difficult to determine the exact point where the effect of the *a*-rays from the radium itself ceases. The effects due to the small amount of emanation and induced activity are always appreciable. If there is any difference, the curves seem to indicate that the power of producing secondary rays is appreciable a little further away from the radium than is the charge. I do not think, however, that we can tell with certainty.

Fig. 3.



Distance from radium to window in cm.
Charge of secondary rays.

Distance from radium to window in cm.
Charge of *a*-rays.

This point is of great importance in connection with the idea advanced by J. J. Thomson, that at a certain velocity the *a*-particle attaches to itself an electron, which neutralizes its charge and therefore changes its properties.

I have tried the above experiments with polonium, but the currents were too small to be satisfactory. I hope to be able to repeat them with a more active preparation of polonium.

Art. XLIV.—*Note on the Alteration of Augite-Ilmenite Groups in the Cumberland, R. I., Gabbro (Hessose)*; by C. H. Warren.

[Contributions to the Geology of Rhode Island.—No. III.]

In a recent paper* descriptive of the geology and petrography of Iron Mine Hill, Cumberland, R. I., it was shown that the basic, titaniferous rock rhodose (cumberlandite) was closely associated with a strongly metamorphosed and altered gabbro, whose areal extent and general characteristics were there described. The rocks taken together formed a roughly circular area of basic igneous rock entirely surrounded by highly metamorphosed, ancient sedimentaries and granite intrusives. The close association of the two rocks, and the fact that both are characterized by a large content of ilmenite, naturally led to a detailed study of the gabbro in connection with that of the rhodose. As a result, it was found that, while the metamorphism and alteration of the gabbro presented many of the common characteristics of such rocks, certain mineralogical changes had taken place, which if previously observed have not been adequately described, and it is the object of the present article to call attention to them.

The unaltered gabbro.—Although the gabbro is nowhere exposed in an unaltered condition, a study of its less highly altered forms shows clearly that it was originally a rather coarse (millimeter) grained gabbro containing, beside abundant augite and accessory apatite, an unusual amount of ilmenite in the form of large irregular grains occurring in close association with augite. The grain of the rock seems to have been generally uniform throughout, although an occasional coarse-grained, almost pegmatitic, development has been noted, as well as a fine (aplitic?) phase. The optical properties of the feldspar indicate a plagioclase of about the composition $Ab_1 An_1$ or a little more acid. The textural relations of the feldspar to the augite and ilmenite is diabasic. In habit the feldspar is strongly tabular on 010, the crystals averaging perhaps almost 1^{cm} square and from 2 to 3^{mm} in thickness. The ore grains, although now more or less reduced in size by alteration, are still large and abundant, many of them averaging as much as 4 or 5^{mm} in diameter. Their distribution seems to have been fairly uniform. Locally, in several places, the grains have been noted larger in size and much more abundant.

On treating a polished surface of the rock with hot hydrochloric acid the ore grains are but slightly attacked, and no such interesting structure (intergrowth of magnetite and ilmenite),

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* This Journal, vol. xxv, Jan., 1908.

as was noted in the case of the ore in the rhodose, was observed. The grains react strongly for titanium and possess a magnetic susceptibility like that of ilmenite. Alteration, as will be pointed out beyond, often develops the characteristic reticulate structure of ilmenite. There can be no doubt, therefore, that the ore in this rock is ilmenite and if any magnetite existed as an original constituent it was very inconsiderable in amount. Occasional flakes of reddish brown secondary mica are present. No indications of any pyroxene, other than augite, or of other original ferromagnesian mineral have been found.

Chemical composition and classification.—For the purpose of showing the chemical character and of classifying the rock quantitatively a single chemical analysis has been made on material taken from a specimen showing relatively the least amount of alteration. The results are as follows :—

Analysis of Gabbro (Hessose).

SiO_2	45·27		
TiO_2	2·77		
Al_2O_3	18·30	Orthoclase	·011
Fe_2O_3	3·30	Albite	·053
FeO	10·13	Anorthite	·104
MgO	4·08	Corundum	·006
CaO	7·32	Hypersthene	·068
Na_2O	3·64	Olivine	·064
K_2O	1·07	Ilmenite	·034
MnO	·86	Magnetite	·021
Co,Ni	tr.	Apatite	·008
P_2O_5	1·27		
S	·08		
H_2O	2·08		
	100·17		
Sp. grav.	2·958		

$$\frac{\text{sal}}{\text{fem}} = \frac{65{\cdot}93}{31{\cdot}53} = 2{\cdot}0,\ \text{Dosalane (2)}$$

$$\frac{\text{Q or L}}{\text{F}} = \frac{0}{65{\cdot}32} < \frac{1}{7},\ \text{Germanare (5)}$$

$$\frac{K_2O + Na_2O}{CaO} = \frac{69}{130} = {\cdot}53,\ \text{Hessose (4)}$$

$$\frac{K_2O}{Na_2O} = \frac{11}{58} = {\cdot}18,\ \text{Hessose (3)}$$

The rock is therefore perfelic, docalcic and presodic, its coordinates in the quantitative system being 2,5,4,3 and may be called a Hessose. It may be noted that the ferrous iron and titanium are both high, and that although the potash amounts to over one per cent no orthoclase has been detected with the microscope. Much of the potash is probably now present in the biotite and sericite.

General megascopic character of the rock.—The entire rock mass has been subjected to more or less severe dynamo- and hydro-thermal metamorphism. The changes thus effected are now somewhat obscured by superficial alteration, but it seems clear that their intensity varied quite irregularly, being stronger toward the northern and northwestern contacts, and in indefinite zones through the body of the mass.

Specimens showing the least metamorphism and but little superficial alteration may be found in the north-central part of the area along an old car track, where the surface of some of the ledges has been blasted away. The rock here is of a dark, greenish brown color, and breaks with a more or less distinct cleavage, owing to a rudely parallel orientation of the tabular plagioclase crystals.

The plagioclase is dark brown in color and is beautifully striated. Between the crystals are irregular patches of dark green or brownish green, finely crystalline, secondary silicates in which are very generally embedded lustrous grains of ilmenite. The green material can be seen to penetrate to some extent the feldspar substance. Polished surfaces, looked at with a good hand lens, serve to show the texture admirably. Outcrops in the southeastern part of the area show about the same degree of metamorphism, although superficial alteration has gone further. On exposed surfaces the feldspar becomes chalky and retreats, leaving the black ore grains and their matrix of secondary silicates, now of a dull, pale green color, standing out in relief.

More severely metamorphosed phases may be recognized by the fact that a portion of the feldspar has changed to a dull white saussurite, a change that becomes complete in the more extreme types. The latter are also characterized by the diminished number and size of the ore grains and by the general loss of the original texture. Types representing these stages may be collected a little east of the exposures of the least altered type above alluded to, and from the ledges on the north and south of the railroad track. Toward the northern border of the area and along portions of the high ridge that forms the eastern outcrop of the gabbro toward the Iron Mine Hill, the rock has lost, so far as its macroscopic appearance is concerned, almost every vestige of its original texture. It shows an indistinct schistose structure, and has a mottled, greenish white appearance. Chlorite, a little sericite and an occasional remnant of ilmenite and feldspar are the only minerals that can be distinctly identified, although the dull white dense groundmass, especially in its weathering, is suggestive of a feldspathic composition. At the contact with the granite and schists on the north, the gabbro has been sheared into a fissile green schist. At the extreme northeast extension of the outcrops the rock has become a greenish white, fissile schist.

Microscopic characteristics of the gabbro—least metamorphosed types.—In addition to this being the least altered of any of the types examined, it may be designated as one whose chief distinguishing features are a large development of secondary biotite and the absence of leucoxenic alteration of the ilmenite. In thin section the feldspar substance is comparatively fresh although occasional patches of sericitic and saussuritic material may be noted, and the crystals are generally characterized by the presence of a brown pigment. The crystals show abundant evidence of mechanical strains.

The augite appears to have been the first constituent that yielded to alteration, and although by far the greater portion of it has gone over to secondary minerals, occasional crystals may still be seen in intermediate stages of alteration. In the thin sections studied, the dominant mode of alteration (if not indeed the only one in this type) is to a more or less confused fibrous aggregate of hornblende. Under low powers this has a cloudy appearance and is of a light yellowish brown color. With higher powers the fibers have a sub-parallel, also somewhat divergent arrangement, and possess in general a pale green or yellowish green pleochroism. The change to this substance begins about the edges, along cleavages or fractures, and encroaches in a quite irregular manner on the augite substance. The amphibole often assumes a distinctly greenish or bluish green color next the plagioclase. Instances may also be noted where the whole aggregate has a more compact texture while at the same time the color is a deeper brown. Small crystals of a yellowish to reddish brown, massive hornblende may also be seen, which are undoubtedly secondary and strongly suggestive of a direct formation from the augite.

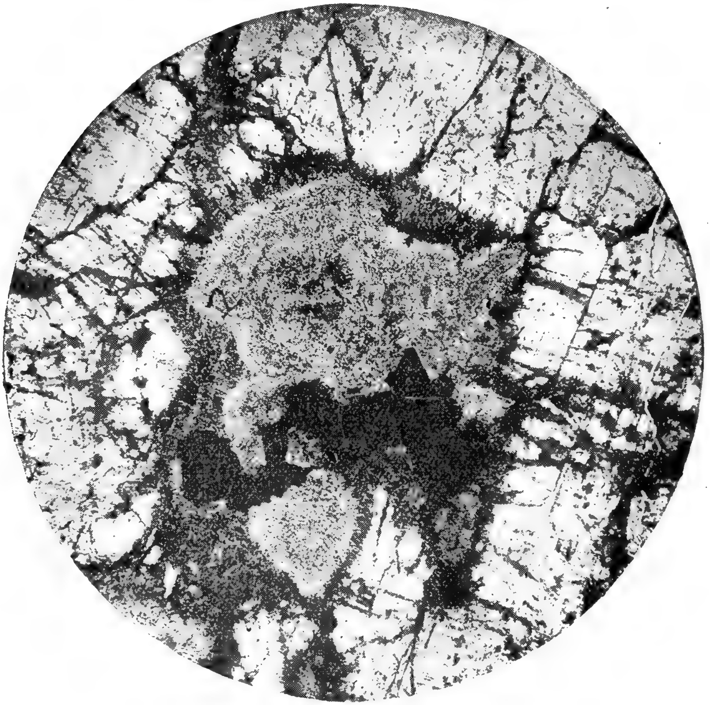
The change of the augite to the fibrous form is followed by a further and more important change, which often begins before the original augite has entirely disappeared and in which are involved reactions with constituents from the ilmenite and plagioclase. The space originally occupied by the augite as well as a part of that occupied by the ilmenite and plagioclase becomes filled with an aggregate composed of hornblende, biotite and particles of ore, the latter largely residual although possibly to some extent secondary. Where augite grains unaccompanied by ilmenite have suffered alteration, biotite is characteristically lacking.

This hornblende is strikingly different in appearance from the fibrous form previously described, and consists essentially of an aggregate of small prismatic crystals and fibers exhibiting a distinct, though not very strong, bluish green pleochroism. Associated with this is a variable amount, often considerable, of hornblende in the form of prismatic crystals of relatively large size and possessed of a strong, bright blue pleochroism, parallel to C. Near the borders of the aggregates they are more abundantly developed, in fact they not infrequently form a distinct border of blue prisms jutting out into the plagioclase. Crystals of hornblende having a yellowish to reddish brown pleochroism parallel to C occur with the blue and appear to have been formed in the same way, indeed the same crystal may show a blue pleochroism in one portion and a brown in another. Both the blue and the brown variety may also be seen, changed, probably by a bleaching process, to a nearly colorless variety. Within the aggregates there appears to be some actinolite.

The biotite is of a light brown color and its formation is clearly connected with the presence of ilmenite. It occurs in part in the form of flakes or shreds mingled with the hornblende. Its amount varies, being most abundant in the neighborhood of the ilmenite, where it not infrequently practically displaces the hornblende. Its most striking mode of occurrence is, however, in the form of a clearly marked border lying between the hornblende and the plagioclase. These borders as a rule practically surround the entire altered area. Their width, relative to that of the area enclosed, varies considerably in different cases but is always large (perhaps from 1/5 to 1/12). The border consists essentially of narrow shreds or flakes, orientated perpendicularly to the contact with the feldspar, into which they penetrate quite irregularly. Blue hornblende (rarely brown) prisms frequently make their appearance in these biotite rims, and, in places, as noted above, may actually constitute a rim themselves.

Needles and stouter prisms of hornblende often accompanied by biotite are abundantly developed along fractures and cleavages in the feldspars, while minute isolated hornblende crystals are to some extent disseminated in many of the plagioclase crystals (gewänderte hornblende). A small amount of calcite and limonite is also present.

Both biotite and hornblende have been noted lying directly in contact with the ilmenite; of the two, biotite seems, however, to be much the most intimately connected as regards formation with the ilmenite. It sometimes forms a continuous crystal about a portion of or even an entire ore grain. In such cases the biotite often contains a considerable amount of included material in the form of minute grains, for the most part opaque but sometimes feebly translucent. Some which show a reddish color are probably rutile. These particles are undoubtedly residual since every gradation between biotite with only a small amount of included matter and that containing a core of massive, unchanged ilmenite, may be seen. It is in fact generally evident from the relations of ilmenite to the secondary silicates, that a very considerable portion of the former has disappeared through reaction. It is to be particularly noted that leucoxenic alteration of the ilmenite is absent in this type. Neither have the oxides of titanium been observed to more than a trifling extent. The appearance of characteristic aggregates of secondary hornblende and biotite with residual ilmenite is shown in the accompanying photograph.



Summary of the mineralogical changes.—After the first change of the augite to the fibrous (or compact) hornblende there appears to have been a profound readjustment of the various constituents of the hornblende, ilmenite and surrounding plagioclase, accompanied by recrystallization and more or less transportation, possibly removal, of material. The particular chemico-mineralogic changes which may be noted here are: 1. The formation of a blue, soda-iron or soda-aluminum amphibole molecule from the soda (and alumina?) of the plagioclase and from the ferric iron of the ilmenite. The brown variety may well be due to the entrance into the molecule of a different proportion of ferric iron and titanium. 2. The formation of biotite, for which both ferrous and ferric iron were derived from the ilmenite, alumina and alkalies from the feldspar, and perhaps magnesium from the augite or fibrous hornblende. The titanium, originally combined with the iron used up in the formation of biotite, probably also enters into this latter mineral; at all events, leucoxene or other titanium-bearing minerals are absent.

The water given off by the rock on intense ignition reacts acid, indicating the presence of fluorine. This is probably present in the hornblende and biotite and it is possible that it may have originally been derived from emanations from the adjoining granite intrusives, which are believed to be later than the gabbro and are known to contain considerable fluorite in places. The effect of even an exceedingly small amount of fluorine in promoting changes like those recorded here would be unquestionably great and is worthy of consideration.

The occurrence of secondary biotite and hornblende about magnetite or ilmenite associated with augite in a manner which appears somewhat similar to the one described here, has been noted very briefly by Mr. S. Allport in an article "On the Metamorphic Rock Surrounding Land's End Mass of Granite, Tolcarn."* Mr. Allport describes brownish spots having the mode of occurrence of magnetite and containing centers of magnetite "surrounded by innumerable minute flakes of brown hornblende or mica, while a short distance is usually green—a fact clearly indicating the diffusion of ferric oxide." Again, "Augite was abundant and has been converted into a brown granular substance." Dr. G. H. Hawes, in "The Mineralogy and Lithology of New Hampshire,† describes and figures magnetite or ilmenite grains surrounded by foliæ of biotite radially arranged in fan-shaped aggregates with the iron oxide as a nucleus, as of very common occurrence in the "syenite" near Jackson, N. H. He expresses the opinion that biotite may be very commonly a secondary product of this kind. Again, Wadsworth‡ recognized it as a secondary mineral developed from magnetite or ilmenite and the surrounding feldspar and more rarely from pyroxene, in some of the gabbros described by him from Minnesota. Dr. Wadsworth also notes its occurrence as a secondary mineral from titanic iron ore and plagioclase in the basic titaniferous rock from Taberg, Sweden, and in the

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* Quart. Jour. Geol. Soc., xxxii, p. 420, 1876. Also referred to and figured by Teall (British Petrography, plate xvii).

† Geology of New Hampshire, C. H. Hitchcock, 1878, Part IV, p. 205, fig. 6, plate xi.

‡ Geol. and Nat. Hist. of Minn., Bull. No. 2, St. Paul, pp. 65 and 90, 1878.

closely similar rock, cumberlandite (rhodose), from the present locality, a fact to which the present writer has more recently again called attention. Its occurrence has also been noted elsewhere, particularly in certain European "Fläscher gabbros." Its development as a secondary mineral jointly from the constituents of ilmenite and plagioclase does not, however, appear to have received much attention in standard works on Petrography, although its importance as bearing on the presence of biotite in metamorphic rocks is obvious.

The effect of superficial alteration of this type is a gradual change of the biotite (to some extent the hornblende) to chlorite accompanied by the formation of epidote. Kaolin, calcite, and limonite also develop.

Second type of altered gabbro.—This type may be characterized, in distinction to the above, as one in which the ilmenite has suffered a leucoxenic alteration as well as a biotitic and hornblendic one, and in which the augite, besides a passage to the fibrous aggregate, shows a direct change to a more or less compact green, or brown hornblende. Specimens of this type have evidently suffered more severely from shearing. The feldspar crystals are frequently crushed and are very generally filled with saussuritic material, in addition to secondary silicates more directly derived from the alteration of the augite and ore. The saussuritic material consists essentially of epidote and zoisite with some muscovite and hornblende.

The change of the augite to the same fibrous aggregate as previously described may be seen clearly and is unquestionably a common one in this type. Another change, sometimes in the same crystal, to a semi-compact pale, bluish green hornblende, which assumes a deeper blue color where it is in contact with the plagioclase, is of frequent occurrence. This hornblende examined with high powers shows an indistinct reedy structure and is filled with minute crystallites of other minerals, iron oxides and epidote chiefly. Irregularly throughout its mass, somewhat divergent fibrous patches may be noted which in color and appearance seem to be identical with fibrous amphibole formed directly from the augite.

These may result directly from the alteration of the green hornblende or perhaps simultaneously with it from the augite. A massive reddish to yellowish brown hornblende may also be seen forming *directly* from the augite. The brown hornblende very often passes sharply in a bright blue variety and also into a practically colorless mineral which seems also to be an amphibole in its character although its double refraction is abnormally low. The fibrous secondary hornblende formed directly from the augite, the green and the brown hornblende, as well as the colorless amphibole, all suffer a further change into a confused aggregate of hornblende prisms exactly like that noted in the previous type. Biotite has also formed in the same manner but both the hornblende and the biotite, particularly the latter, have suffered a more general distribution through the rock and are less closely confined to the place of original formation. Much of the biotite and hornblende has now suffered further alteration to chlorite.

Leucoxene is abundantly developed about the ilmenite and is plainly of later origin than the biotite and hornblende. It is distinctly crystalline and has the characteristics of titanite. This leucoxenic alteration has brought out with great clearness the reticulate structure of the ilmenite.

In comparing what have here been called the two types of alteration, the writer is led to conclude that the former is one brought about under conditions of deep-seated, hydrothermal action but unaccompanied by extreme shearing and crushing. In the second type generally similar changes obtained for a time but were succeeded by others induced by more severe local dynamic action. The latter changes are: The formation of leucoxene; a greater tendency for the augite to pass directly into a compact or semi-compact hornblende; increased saussuritization of the feldspar; and a more general distribution of the secondary hornblende and mica throughout the rock.

More highly metamorphosed types.—Further metamorphism and alteration of the gabbro presents little that is novel, and a very general statement will suffice. The microscope reveals increased crushing and saussuritization of the feldspar, a complete change of the hornblende and biotite to chlorite and epidote, an almost complete alteration of the remaining ilmenite to leucoxene, and the development of some sericite. Some secondary quartz and recrystallized feldspar may also be noted. A more or less schistose arrangement of the constituents becomes evident and the outlines of the original structures are less and less distinct, until in extreme phases, from near the northern contacts, the slides show little more than a schistose mass of finely crushed feldspar mingled with secondary products.

Laboratory of Mineralogy and Petrology,
Massachusetts Institution of Technology, Boston, Mass.

ART. XLV.—*Studies in the Cyperaceæ;* by THEO. HOLM.—XXVI. Remarks on the structure and affinities of some of Dewey's *Carices*. (With 24 figures drawn from nature by the author.)

AMONG the circa eighty *Carices*, which Dewey described, there are some which have proved very troublesome to caricologists. The diagnoses are not always so complete or exact as they might have been written; or the material on which certain species were founded was not quite mature, thus the reader does not always receive a very clear impression of the most essential characteristics of some of these species, even if they may be perfectly distinct and valid. In such cases, where we cannot depend entirely upon the diagnosis, the examination of Dewey's own specimens may, sometimes, be helpful. But unfortunately the material left by Dewey is not only small, but it contains, moreover, specimens which are not all in conformity with his diagnosis, and such specimens must consequently not be looked upon as his original, those on which he founded his new species. The best set of Dewey's species is in the herbarium of Kew; these specimens were named by Dewey himself and presented to Boott. There is, furthermore, some material at present incorporated in the Gray herbarium at Cambridge, which is very valuable so far as we are able to distinguish between those plants that were parts of his original specimens and others, which he simply identified as being identical, but which, sometimes, are very different species. Dewey did not work with types, he worked with species, and naturally expected that his species were to be identified by means of the diagnoses. It would be very unsafe and unjust to give preference to the specimens in case of determination, instead of to the diagnosis. When Dewey's specimens do not agree with the diagnosis, we may feel sure that they were not correctly named. Much confusion has arisen from the attempt of certain authors to identify species by means of "supposed types," especially when a critical examination of the diagnosis necessarily must convince us that said specimens were not the original, not the one on which the species was established. The interpretation of Allioni's *Carex fusca* and *bipartita* is a good example of the result of this kind of verifying old specimens,* but several other cases might easily be recorded.†

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* This Journal (4), vol. xvi, p. 145, Feb., 1903.

† The following note, copied from a letter received from Mr. Clarke, may be of interest to the reader: "Willdenow did not work from types but from small packets (now largely sorted into different species in the Berlin Herb.). You can see this, because Kunth repeatedly cites Willd., folio 2 or folio 3, for species which he sets up as new (or separate). Feb. 24, 1902."

Now in regard to Dewey's species, it is our intention to demonstrate that some of these have been misunderstood; that some of these are not so difficult to identify, if we give preference to the diagnoses, and not to the specimens extant. It appears to the writer that the reprinting of the original diagnoses may be necessary, inasmuch as some of these are not known to several caricologists, who have no access to the earlier volumes of this Journal, in which they were published. But whatever importance may be attached to the present supplemental notes on these species, we must not forget to mention that we owe much information to a prolonged correspondence with the late cyperographer C. B. Clarke of Kew, who was so very familiar with the large herbarium of Boott and many others. The modern method of identifying species by means of "supposed types" was, according to Clarke, a most dangerous experiment, since in particular respect to *Carices* neither Dewey nor Boott worked with types. In a note on *Carex Tolmiei* Boott,* Clarke has shown how very difficult it may be, sometimes, to reach an exact conclusion even from a work so excellently written and illustrated as that of Boott: Illustrations of the genus *Carex*.† The species of Dewey which we intend to discuss are: *C. petasata*, *C. Barbaræ*, *C. magnifica*, *C. Schottii*, *C. petricosa* and *C. mirata*. Of these *C. petasata* has been suppressed entirely, as will be shown in the subsequent pages; *C. Barbaræ*, *C. Schottii* and *C. mirata* have either been referred to other plants, or have been merged into each other as synonyms; *C. magnifica* was never described, but mistaken for *C. Sitchensis* Prescott, while *C. petricosa* was known only from very immature specimens. With the exception of *C. Barbaræ* of which there is no material in Kew, but in Cambridge, we have had the opportunity to compare the others with authentic specimens, authentic to the full extent of the word, since they were in accordance with the original diagnoses; this material was made accessible to the writer through the kindness of Mr. Clarke. In regard to *C. Barbaræ* a young, but nevertheless quite complete, specimen named by Dewey in the Gray herbarium was loaned to the writer; beside that we succeeded in finding some mature specimens of this very rare species in the collections of Mr. Parish, now deposited in the U. S. National Museum.

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* Journ. Linn. Society, vol. xxxv, p. 403.

† "Boott has named in his own hand many *Carices* in the herbarium and *X* takes these as 'authentic'; but they are, in very many cases, authentically wrong. In his herb. propr., Boott usually pasted down, all mixed together, 3, 4 or even 7 collections on one sheet. His figures often include utricles from several collections, to show his idea of the range of variation 'in each species.' If, however, the utricle varied really to the degree he depicts it, it would be of very little use in diagnoses of species" (C. B. Clarke in litteris, Oct. 11, 1899).

Carex petasata Dew.

According to Professor Bailey (l. c. p. 52) "the original sheet of this species is in Herb. Torr. It contains three plants: *C. lagopina* Wahl., *C. festiva* Dew., and *C. Liddoni* Boott, to all of which Dewey's description will equally apply." For this reason Professor Bailey does not think that *C. petasata* "can be pressed into service," and although as he states himself, "*C. Preslii* is not clearly accounted for," and "the original does not exist, either in the collection of Presl or Steudel," he nevertheless adopts Steudel's name "in lieu of any other." It may be that the specimens in Torrey's herbarium were mixed, but there are several good examples of *C. petasata* in Boott's herbarium, received from Dewey and authenticated by his hand, and Mr. Clarke has informed us that these specimens are not mixed. Consequently there is no reason why the name *petasata* should not be retained for this species, and the diagnosis written by Dewey* reads as follows:

"Spicis distigmaticis androgynis, inferne staminiferis subquaternis ovato-oblongis cylindraceis subsessilibus approximatis; fructibus lato-lanceolatis utrinque acutis rostratis vel acuminatis ore bifidis subalatis, squama lato-ovata subobtusa longioribus. Culm 4–8 inches high, erect, slightly scabrous, triquetrous, striate; leaves shorter below, upper one about as long as the culm; spikes androgynous staminate below, oblong cylindric, about 4, short pedunculate, approximate, brownish; fruit broad lanceolate, acute at each end, acuminate or rostrate, compressed, bifid and slightly winged, convex above; scale ovate, obtusish, tawny, broad, shorter than the fruit. Found on the Rocky Mountains."

Characteristic of the species is, thus, the ovate-oblong spikes, which are short peduncled and approximate, but not sessile, forming a head; moreover the broadly lanceolate perigynia tapering at both ends, and narrowly winged. Frequently the spikes, especially the lower ones, are somewhat remote, very distinctly peduncled and subtended by setiform bracts, thus resembling *C. pratensis* Drej.—The perigynia are light brown and faintly, though very distinctly, veined (about six veins on the outer face). It would consequently be very unjust to consider the specimens in Torrey's herbarium as being Dewey's type. In the first place because Dewey did not work on types, and secondly because his diagnosis by no means applies to the three species which Professor Bailey found in said herbarium. This may be readily seen from the fact that so far as concerns *C. lagopina*, the perigynia of this species are ovate to almost round, and never winged; in *C. festiva* the spikes form a

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* This Journal (1), vol. xxix, p. 246, 1836.

dense head, and the perigynia vary from ovate to suborbicular, broadly winged and prominently veined; in *C. Liddonii* the very heavy spikes and large perigynia, which are many-nerved and with prominently serrulate-winged margins, make this species very distinct from *C. petasata.* In regard to the geographical distribution *C. petasata* has been found in Alaska, but only in a few localities; furthermore and apparently frequent in the mountains of Washington, Oregon and Idaho, in the Alpine regions; it occurs, also, in British Columbia, Alberta, Assiniboia, Vancouver Island, Montana, Wyoming, Utah and Colorado; it seems to be rare in Colorado, and is there confined to the highest peaks above timber-line.

Carex Barbaræ Dew.

Through the kindness of Mr. M. L. Fernald the writer has had the opportunity to examine probably the only specimen extant from Dewey's own material of this very rare species, deposited in Wm. Boott's herbarium, now incorporated in the Gray herbarium at Cambridge. It is an immature specimen, but labeled by Dewey himself: "*C. Barbaræ*, Santa Barbara, New Mexico," and the principal characteristics are easily recognized to be in conformity with the diagnosis, as this was written by Dewey.* Subsequent authors have not, however, paid due attention to the original diagnosis, for instance, the peculiar structure of the squamæ, and the result has been that *Carex Barbaræ* of to-day comprises several distinct species, among which Dewey's *C. Schottii* and *C. dives* nob. While thus the specimen, which we have examined, is immature, the diagnosis plainly shows that Dewey based his description on more perfect and mature specimens; if not he would have said so, for he was careful enough to state in his diagnosis of *C. Schottii* that the perigynia were either wanting or immature. To deal with immature specimens of *Carices* especially is a most difficult task, but, in the present case, we have a well written diagnosis beside a specimen labelled by the author himself. It seems very strange that so much confusion should arise in regard to the identity of this species, since the group of *Carices* to which it belongs is rather poor in representatives, and, as stated above, so very distinct from that to which the other plants belong, which erroneously have been referred to *C. Barbaræ.* From reading Dewey's diagnosis there is absolutely no doubt that his *Carex* is a member of the *Æorastachyæ*, and related somewhat to *C. Schottii* and *C. magnifica*, which he distributed under this name though without appending a diagnosis. Most of the species which subsequent authors

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* Emory's Report U. S. and Mex. Bound. Survey, p. 231, 1858.

have named *C. Barbaræ* are members of the grex *Microrhynchæ*, and more or less closely related to Prescott's *C. Sitchensis.* It seems a strange coincidence that this species of Prescott should suffer the same fate as *C. Barbaræ*, to become so entirely misunderstood for many years, although the diagnosis plainly shows us that it was not intended for the very characteristic *C. magnifica* of Dewey. When thus modern caricographers consider *C. Barbaræ* to be a close ally of *C. aquatilis* Wahlenbg., we are now in the position to state that it is not by any means related to this, neither to this particular species, nor to any of the other members of the *Microrhynchæ.* Inasmuch as the real *C. Barbaræ* seems to be a very rare plant (not represented in any of the large herbaria at Kew) it might be appropriate to reprint the original diagnosis, and to give an account of the confusion into which the species has fallen. Dewey's description reads as follows: "*Carex Barbaræ* Dewey: spicis staminiferis terminalibus 2 raro 3 erectis cylindraceis, suprema longe pedunculata, inferiore breviore illi contigua, infima sub-elongata; pistilliferis 3 longo-cylindraceis, 2–4 uncialibus gracilibus, superiore apice staminifera brevibracteata erecta, inferioribus, longioribus, subremotis, subrecurvis basi laxifloris brevi-vaginatis foliaceo-bracteatis, omnibus nigro-purpureis, perigyniis distigmaticis oblongis obovatis apiculatis ore integris, squama oblongo obovata dorso pallida mucronata brevioribus; culmo erecto glauco longe-foliato vaginatoque. Banks of streams, Santa Barbara, California; Parry.—Culm 16–20 inches high, erect, with long leaves towards the base and long leafy bracts above, glaucous; spikes 3–6, cylindric, slender, blackish purple; staminate terminal 1–3, commonly 2, the upper nearly two inches long, pedunculate, the lower sessile, contiguous and shorter, the third longer than the last and more remote; pistillate 3, long cylindric, 2–4 inches long, slender; the upper staminate at the apex, short-bracteate, erect; the lower longer, subremote, subrecurved, loose-flowered at the base and short-sheathed; perigynium oblong-obovate, short-rostrate, entire at the orifice, stigmas 2, pistillate scale oblong-obovate, on the back pale, and the nerve extended into a mucronate point, making the end of the scale sometimes emarginate. The locality gives the name of the species." Some mature specimens of *C. Barbaræ* Dew. have been collected by Mr. Parish in San Bernardino Mountains,* and by examining these we noticed that the perigynia exhibit several very fine nerves, which must have been overlooked by Dewey; otherwise these specimens showed exactly the same habit and structure of squamæ as Dewey's own specimen. It is to be

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* Southern California, alt. 3000 ft., S. B. Parish, No. 3276, deposited in the herbarium of U. S. National Museum.

remembered that the minor structure of the perigynium in *Carex* is seldom noticeable in the dried state, but readily visible in fresh material or by soaking the dried specimen in boiling water and alcohol. In pointing out some of the most striking characters of this species we might mention: the long and slender, blackish purple spikes, the oblong-obovate, mucronate squamæ, sometimes emarginate, which are longer than the faintly nerved, oblong-obovate perigynia; furthermore the short beak with entire orifice.

Let us now consider some of the other plants which formerly have been referred to *C. Barbaræ*, but which we believe are distinct from this. There are, for instance, in the Gray herbarium some specimens, and very well represented, of a *Carex*, which are named *C. Barbaræ* in Dewey's own handwriting; they are from Hayden's collection and the localities are given as: "Lake Fork, 6,000 ft. above the sea, also on Madison River," "and near Fort? (the name written very indistinctly), high on Rocky Mountains." A note attached to these specimens and signed S. T. O. (Stephen T. Olney) reads: "These specimens are unlike those so named in Mex. Bound. Survey. Doctor Dewey had marked one of these (the former) *C. stricta* Good., to which they possibly belong." We can only agree with Olney that these specimens are quite distinct from *C. Barbaræ vera*, but we prefer to place them under *C. Nebraskensis* Dew. var. prævia Bail. In his treatment of *Carex* in King's Report,* Olney referred *C. Barbaræ* to F. Boott's *C. Prescottiana*,† as a synonym, but Boott's species is very different from that of Dewey; it, also, deserves notice that Olney in the same paper refers *C. Sitchensis* Dew. not of Prescott as synonym of *C. laciniata*, which shows very plainly that Olney was not acquainted with the real *C. Sitchensis* Presc., but that he mistook *C. Sitchensis* Boott for this species, while Dewey segregated Hooker's and Boott's *C. Sitchensis* as his *C. magnifica*. Another specimen which is also incorporated in the Gray herbarium is by Dewey labelled *C. Sitchensis* Presc.; it was collected by Professor Wood in swamps near Los Angeles, California. This specimen differs from *C. Barbaræ* by the pistillate squamæ being merely acute, the midvein being not excurrent, besides by the shortness of the scales in proportion to the perigynium; from typical *C. Sitchensis* this specimen differs only by the presence of a few, faint nerves on the outer face of utriculus. Professor Bailey has, nevertheless, identified this plant as representing *C. Barbaræ*. While Mr. Parish had the good fortune of rediscover-

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* U. S. Geol. Explor. of the 40th Parallel, p. 361, 1871.

† Caricis species novæ, vel minus cognitæ. (Transact. Linn. Soc., vol. xx, p. 135, 1845-46.

ing the rare *C. Barbaræ*, as stated above, he has also collected another species of very robust habit, which, however, does not appear identical with Dewey's plant. As a matter of fact, this tall *Carex* distributed as *C. Barbaræ** resembles much more the real *C. Sitchensis* Presc., but the perigynia are distinctly nerved, very large, and considerably longer than the squamæ. If the perigynia had been smaller, merely two-nerved and scabrous along the upper margins, the species might have been referable to *C. dives.*

In the herbarium of the U. S. National Museum we found several specimens identified by recent authors as *C. Barbaræ* Dew., but only the specimen mentioned above, collected by Mr. Parish (No. 3276) and some immature ones from Sanger, Fresno county, California, collected by Dr. J. W. Hudson, represent this species; the others were *C. amplifolia* Boott, *C. Schottii* Dew., *C. laciniata* Boott, etc.

As received by Professor Bailey† *C. Barbaræ* should be identical with *C. Schottii* Dew., which actually is *C. obnupta* Bail., furthermore with the plant which Dewey himself had called *C. Sitchensis*, and with a third species from Washington and Vancouver Island, which by the writer has been described as *C. dives.*‡ The fact that Professor Bailey considers *C. Barbaræ* a close ally of *C. aquatilis* Wahl. is a sad illustration of how easily a good species might be lost sight of; because none of the allies of *C. aquatilis* Wahl. possess squamæ and perigynia of the structure as is characteristic of *C. Barbaræ.* We must admit, however, that the structure of both squamæ and perigynia is somewhat variable in a number of *Carices*, and especially among *Carices genuinæ;* the nervation of the perigynium is not always equally developed, and the apex of the squama may vary from acute to mucronate or even aristate. But, on the other hand, we do not remember a single instance where within the same species the apex of the squama varies from obovate, mucronate and sometimes emarginate to oblong-lanceolate and simply pointed; for this reason the writer does not feel inclined to remodel the original diagnosis of *C. Barbaræ* in order to include the several more or less distinct species, as has been done by recent authors. According to our opinion, the specimen of Dewey's own collection and those of Mr. Parish (No. 3276), which we have cited above, these are sufficiently instructive for demonstrating the species as understood by Dewey; all the other plants must be referred to other species.

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* Southern California: Damp land, meadows or swamps, alt. circa 300 m. San Bernardino Valley, No. 5981, March 9, 1907.

† Memoirs Torrey Bot. Club, vol. i, p. 44, 1889.

‡ This Journal (4), xvii, p. 312, 1904.

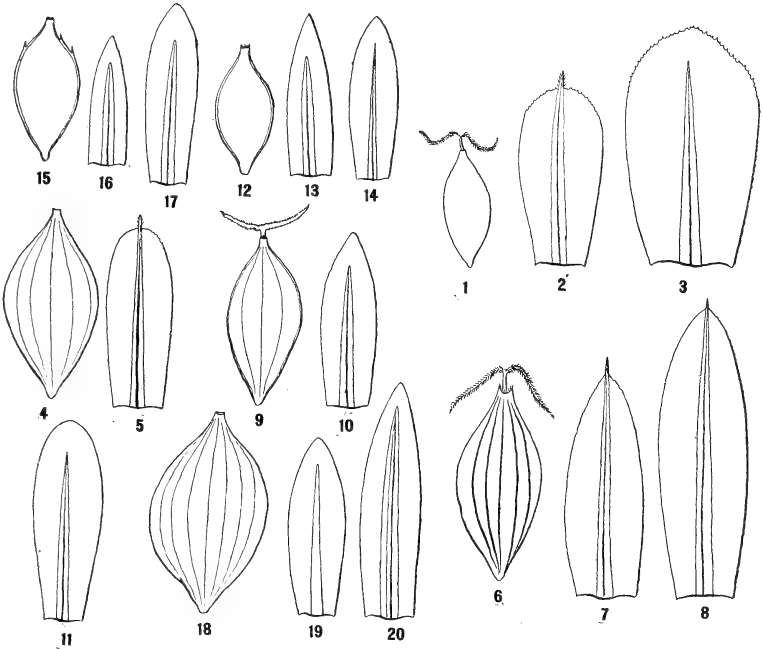

Fig. 1, perigynium; fig. 2, pistillate scale; fig. 3, staminate scale of *Carex Barbaræ* Dew., from St. Barbara, identified by Dewey.

Fig. 4, perigynium; fig. 5, pistillate scale of *C. Barbaræ* from San Bernardino Mts., collected by Parish (No. 3276).

Fig. 6, perigynium; fig. 7, pistillate scale; fig. 8, staminate scale of *C. Nebraskensis*, from Lake Fork, collected by Hayden.

Fig. 9, perigynium; fig. 10, pistillate scale; fig. 11, staminate scale of *Carex sp.*, by Dewey identified as *C. Sitchensis* Prescott from Los Angeles, collected by Wood.

Fig. 12, perigynium; fig. 13, pistillate scale; fig. 14, staminate scale of *C. Sitchensis* Presc. from Sitka, collected by C. V. Piper.

Fig. 15, perigynium; fig. 16, pistillate scale; fig. 17, staminate scale of *C. dives* Holm from Chilliwack Valley, collected by James M. Macoun.

Fig. 18, perigynium; fig. 19, pistillate scale; fig. 20, staminate scale of *Carex sp.* from San Bernardino Valley, collected by Parish (No. 5981), and described as *C. Barbaræ* (Bull. South Calif. Acad. of Sc., p. 108, 1905).

The accompanying drawings (figs. 1–20) illustrate perigynia and scales of *Carex Barbaræ* Dewey, and of some other species which by subsequent authors have been referred to this species. It is readily to be seen that the figures of Dewey's own but immature specimen (figs. 1–3) agree very well with those collected by Mr. Parish (figs. 4–5); furthermore, that Dr. Hayden's specimens from Lake Fork (figs. 6–8) are undoubtedly *C. Nebraskensis* Dew. Then there is the plant which Dewey himself identified as *C. Sitchensis* Presc. (figs.

9–11), and which Professor Bailey has referred to *C. Barbaræ*. By comparing these figures with those of *C. Barbaræ* (figs. 1–5), it seems not very difficult to see that they are not the same species. Dewey's specimen of *C. Sitchensis* agrees well with the Sitka-plant (figs. 12–14), with the only difference that the latter lacks the nerves in the perigynium. In figs. 15–17, we see the perigynia and scales of a *Carex* from British Columbia, which Professor Bailey has also referred to *C. Barbaræ;* this northern plant we have described as *C. dives*, and it is certainly very distinct from *C. Barbaræ* Dew., but a near ally of *C. Sitchensis* Presc. Finally we have the very robust species from Mr. Parish's collection (figs. 18–20), and this cannot possibly be identified as *C. Barbaræ* Dew. either; it may represent an undescribed species, unless it be a gigantic *C. Sitchensis* Presc.

In regard to *C. Sitchensis* Presc. we might state at the same time that our figures 12–14 were drawn from some material collected recently by Professor C. V. Piper, and that these specimens agree in all respects with authentic material in Bischoff's herbarium, which is now in the possession of the St. Louis botanical garden.

Carex Barbaræ Dew. must be placed among the *Æorastachyæ* Drej. on account of the long, nodding, dark-colored spikes, the broad mucronate scales and the glabrous perigynia with the orifice entire.

Carex magnifica Dew.

As stated in a previously published paper,* this species has for many years passed for *C. Sitchensis* Prescott, and described and illustrated by Boott† as representing this species. Several specimens were sent to Boott by Dewey under this name *magnifica*, but not accompanied by any diagnosis; however, there being no other name or synonym for it, the name *magnifica* has been adopted by C. B. Clarke, and we now append the diagnosis, copied from Boott (l. c.) and based upon specimens from California:

"Spicis 5–8 cylindricis atro-purpureis, masculis 2–3 rarius 4 sessilibus erectis, foemineis 3–5 superioribus conspicue (raro omnibus) apice masculis inferioribus pedunculatis erectis vel nutantibus evaginatis basi saepe laxifloris; bracteis inferioribus culmum superantibus; stigmatibus 2; perigyniis ovalibus v. obovatis vel subrotundis rostellatis biconvexis, ore integro glabris vel ad margines apice subinde parce denticulatis flavidis dense spongiosis, squama ovato-lanceolata acuminata acuta

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* This Journal, vol. xvii, p. 316, April, 1904.

† Ill. genus *Carex*, vol. iv, p. 159, Pl. 518 and 519.

vel aristata saepe obtusa pellucida lineata, angustioribus duplo brevioribus."

This species has been collected in Alaska, British Columbia, Vancouver Island, Washington, Oregon and California; it grows in marshy ground, on borders of ponds, etc., and ascends to an elevation of 3,500 feet in the Olympic mountains.

Carex Schottii Dew.

The latest disposition that has been made of this species is to regard it as identical with *C. Barbaræ* Dew., a suggestion proposed by Professor Bailey.* But from the statement by this author that *C. Barbaræ* is closely allied to *C. aquatilis* Wahlenb., it is evident that Professor Bailey has not had access to authentic material; moreover, the specimens cited from Vancouver Island and Washington do not agree at all with the diagnosis of *C. Barbaræ* or of *C. Schottii.* On the other hand, the plant described as *C. obnupta* by Professor Bailey† is the real *C. Schottii* Dew.

The diagnosis as written by Dewey‡ reads as follows:

"Spicis staminiferis terminalibus 3–5 erectis nigro-rubris approximatis prope geminatis cylindraceis, superiore longa 3--unciali medio inflata, inferioribus brevioribus sessilibus contiguis vel infima remotiore et interdum geminata; pistilliferis 3 raro 4 perlongo-cylindraceis gracillimis 6–8 uncialibus perlaxifloris inæqualiter pedunculatis, inferioribus longe pedunculatis folioso-bracteatis basi vaginatis vix fructiferis vel abortivis, cum squamis oblongis arctis obovatis vix acutis; perigynio carente vel nimis immaturo; culmis superne scabris subprostratis cum foliis bracteisque viridi glaucis. Banks and rivers, Santa Barbara, California; Parry."

Since then the species has been collected by Bolander (No. 1570) in salt marshes near Fort Point, Golden Gate, California, and in these specimens the perigynia are mature; the late Mr. C. B. Clarke identified Bolander's specimens and it was through his kindness that the writer received mature specimens so as to ascertain the identity of Professor Bailey's *C. obnupta* with the present species of Dewey. In *Carex Schottii* the perigynia are shining, dark reddish brown, orbicular, shortly stipitate, glabrous, or with a small spine near the short, entire beak; the perigynium is much shorter than the oblong-lanceolate, pointed scale.

The species is a near ally of *C. magnifica*, possessing the same very dark-colored spikes, the coriaceous perigynia, which are more or less orbicular and much shorter than the squama.

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* Memoirs Torrey Bot. Club, vol. i, p. 44, 1889.

† Proceed. Calif. Acad., vol. iii, p. 104, 1893.

‡ Emory's Report U. S. and Mex. Bound. Survey, p. 231, 1858.

Carex petricosa, Dew.*

The original diagnosis† reads as follows:

"Spicis subquaternis oblongis tristigmaticis, terminali androgyna superne staminifera, inferioribus exserte pedunculatis; fructibus lanceolatis lævibus acutis ore apertis, squama ovato-oblonga obtusiuscula brevioribus.

Culm ten inches high, triquetrous, smooth, leafy towards the base, upper leaves as long as the culm; bracts leafy and sheathing; spikes four, exsertly pedunculate, oblong, subremote; fruit lanceolate, smooth, with an open mouth; stigmas three, and upper spike staminate above; pistillate scale ovate, oblong, rather obtuse and longer than the fruit, reddish brown on the edge and whitish on the keel. Found on the summit of the Rocky Mountains."

FIG. 21. Fruiting specimen of *Carex petricosa* Dew.; one-third of the natural size.

FIG. 22. The inflorescence of another specimen with five spikes; one-third of the natural size.

FIG. 23. Pistillate squama of same; magnified.

FIG. 24. Perigynium of same; magnified.

The specimens were collected by Drummond between lat. 54°–56°, and according to Macoun‡ the locality must have been between the sources of the Athabasca and Peace River. For many years the species was lost, and it is not until very recently that this very rare and interesting species has been

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* = C. invisa Bailey.

† This Journal (1) xxix, p. 246, 1836.

‡ Catalogue of Canadian plants, Montreal, p. 138, 1888.

rediscovered. Mr. N. B. Sanson found the plant on Rundle Mountain near Banff in Alberta, at an elevation of 6,000 feet, and growing together with *Carex rupestris* All. Through the kindness of Mr. James M. Macoun the writer has received an excellent suite of fully matured specimens, in which we have observed some characters which are not mentioned by Dewey; we remember that the material which Dewey described was not quite mature and only scantily represented.

One of the most striking peculiarities in this species is the manner in which the staminate and pistillate flowers are distributed. The number of spikes varies from two to five, but four seems to be the most frequent. As indicated in the diagnosis "spica terminali androgyna superne staminifera" Dewey did observe that both sexes were present in the terminal spike; however he makes no mention of the other spikes, which he evidently took to be pistillate, as is the most frequent in this group of *Carices*. While thus an androgynous terminal spike appears to be typical of this species, it deserves notice that this spike is wholly staminate in small specimens. In regard to the other spikes the distribution of the sexes varies somewhat, and may be illustrated by the following table:

Terminal spike: mostly androgynous, seldom purely staminate.
Uppermost lateral spike: staminate, very seldom pistillate.
Second lateral spike: pistillate or androgynous, very seldom staminate.
Third lateral spike: pistillate, very seldom androgynous.
Fourth lateral spike: pistillate, very seldom androgynous.

There is thus a tendency of having the staminate flowers situated in a single spike below the androgynous terminal, while the subsequent spikes are mostly pistillate or, sometimes, androgynous. Such irregularities in regard to the disposition of the flowers are not, however, uncommon in various greges of the genus.

To the original diagnosis may, furthermore, be added that the perigynium (fig. 4) is hairy above and distinctly nerved (six or seven nerves on the outer face) when mature; the orifice is whitish, slit on the outer face, but entire on the inner. When fully mature the perigyninm is longer than the scale. As may be seen from the accompanying drawing (fig. 1) the rhizome is stoloniferous, and the slender culms are longer than the leaves; the basal spike is long-peduncled and drooping, while the others are sessile and appressed to the culm.

The internal structure, which agrees with that of several of the other mountain species, may be briefly described as follows:

The roots have no exodermis, but the cortex shows three very distinct zones : a peripheral, thin-walled and solid, inside of which are three strata of slightly thick-walled stereome, surrounding an inner broad parenchyma of irregularly collapsed cells. Endodermis is moderately thickened all around, and the same structure occurs, also, in the pericambium, which is almost continuous, i. e. only interrupted by two of the twenty-four proto-hadrome vessels. The leptome-strands are distinct, but very narrow. Inside the proto-hadrome are twenty wide scalariform vessels, which surround a broad central mass of thick-walled conjunctive tissue.

The culm is obtusely triangular, glabrous and hollow; the cortex represents a very compact parenchyma of roundish cells, but without palisades, and is interrupted by the stereome, which occurs as hypodermal strands bordering on the leptome-side of the mestome-bundles. These are arranged in a single triangular band surrounding a thin-walled pith, of which the cell-walls show very distinct spiral thickenings.

The leaves are narrow, but flat, scabrous only on the ventral face from minute warts; the stomata, which are confined to the dorsal face of the blade, are level with epidermis and have a wide but shallow air-chamber. Wide lacunes traverse the chlorenchyma, in this species differentiated as a ventral palisade, and a dorsal pneumatic tissue of irregularly branched cells; there is, furthermore, a single layer of palisades around each vein, radiating toward the center of these. The stereome is not very thick-walled and occurs as hypodermal strands and bordering on both faces of the veins; no isolated strand of stereome was observed in the leaf-margin. All the mestome-strands show the usual structure, being collateral and surrounded by a parenchyma- and a mestome-sheath. Although the plant grows in very dry, stony soil, the leaves have no water-storage tissue, but are able to close by means of a longitudinal band of typical bulliform cells, which are located above the midrib, on the ventral face of the blade.

The anatomy of the *Stenocarpæ* to which our species belongs has been discussed by the writer in a previously published paper.* When comparing *C. petricosa* with these species it will be seen that its root-structure is quite different, since in the other species an exodermis is developed, besides that the peripheral strata of cortex are stereomatic, while in *C. petricosa* the stereomatic zone is located almost in the middle of the thin-walled cortex. The interruption of the pericambium by the proto-hadrome vessels is, on the other hand, a character that is common to most of these species.

An obtusely triangular and glabrous culm is seldom met with in this grex but has also been observed in *C. ablata*. In regard

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* This Journal, (4), x, p. 278, Oct., 1900.

to the leaf the structure agrees best with that of *C. ferruginea*, in which a typical palisade-tissue is developed; but while all the species examined possess an isolated strand of stereome in the leaf-margin, this was not observed in *C. petricosa.* The free position of the stomata being level with epidermis and not covered by papillæ is a structure which seems to be frequent among the *Stenocarpæ* even if most of these are inhabitants of dry soil among rocks; we have shown in the paper, cited above, how very little may be depended upon the structure of the stomata as indicating the nature of the habitat. Moreover, this same free position of stomata was, also, observed in *C. rupestris*, which, as stated above, was found associated with *C. petricosa.*

Carex mirata Dew.

In a preliminary synopsis of North American Carices Professor Bailey* has referred this species to *C. aristata* R. Br., and in a subsequent paper by this same author† no further mention is made of this particular species. But we find in the latter of these publications a new species called *C. exsiccata* Bail., said to be a near ally of *C. vesicaria* L., though "in some of its forms strongly suggestive of *C. trichocarpa* Muehl, var. *aristata* (R. Br.) Bail." No diagnosis is given, only the brief remark that *C. exsiccata* "differs at once from *C. vesicaria* by its greater size and broader leaves, thicker and more nearly sessile spikes, and particularly by the much longer, lance-ovate, scarcely inflated, duller and strongly nerved perigynium, which is three to four times longer than the very narrow and muticous scale," besides, as stated above, that it suggests *C. aristata* R. Br.; some varieties of *C. vesicaria: globosa* Olney, *major* Boott and *lanceolata* Olney are referred to this new species (*C. exsiccata*) as synonyms.

Since then no suggestion has been offered as to the validity of Dewey's species, and the fact that Professor Bailey failed to append a diagnosis to his new species (*C. exsiccata*), would naturally result in a possible confusion of both species, since Dewey's diagnosis calls for a plant which is not so very remote from *C. vesicaria.* Some few years ago, when the writer was engaged in the preparation of a paper on "Greges Caricum," Professor C. Piper kindly called our attention to the fact that Dewey's diagnosis was very well applicable to a number of authentic specimens of *C. exsiccata* Bail.

Carex mirata was first described in Wood's Botany (1848), and although Carey‡ had not seen the plant, he nevertheless recognized it as a distinct species, placing it between *C. Pseudocyperus* L. and *C. hystricina* Willd., quoting Dewey's diagnosis, and giving the geographical range as: Shore of Lake

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* Proceed Am. Acad. of Arts and Sci. p. 75, 1886.

† Mem. Torr. Bot. Club, l. c., p. 6.

‡ Gray's Manual, New York, p. 531, 1857.

Ontario, in Monroe County, New York, collected by Dr. Bradley. A more complete diagnosis was given by Dewey in 1865,* which reads as follows:

"Spicis 3–5, longo-cylindraceis incluse pedunculatis longe-folioso-bracteatis; spicis staminiferis, 1–3 sæpe 2, approximatis interdum ad basin vel erga apicem pauco fructiferis cum glumis longis arctis attenuatis scabro-subulatis; spicis *pist.* 1–2, laxifloris suberectis subremotis ad apicem vulgo staminifera; fructibus parvi-ovatis longo-conicis vel lanceolatis vix inflatis nervosis vel striatis longo-stipitatis divergentibus rostratis, rostro profundi-fisso bicuspidato interdum bifurcato vel bidentato; glumis fructiferis lineari-lanceolatis scabro-subulatis, fructu superno spicæ brevioribus, fructum inferiorem æquantibus, atque fructus infimos plus duplo superantibus: culmo superne scabro, inferne obtusi-triquetri et lævi; foliis bracteisque nodosis et margine scabris."

It is to be regretted that Professor Bailey has not described his *C. exsiccata* in any other way than, as stated above, by merely alluding to the distinctive characters when compared with *C. vesicaria* L., and this is not a diagnosis. However, the writer has had the opportunity of examining several specimens identified by Professor Bailey himself as representing *C. exsiccata*, and these specimens not only answer the diagnosis of *C. mirata* Dew. in most respects, but they agree, furthermore, with some authentic specimens from Dewey's own collection. When we use the expression "in most respects," we wish to say that there are some points in Dewey's diagnosis which we have not been able to observe in the specimens. This is for instance the case with "fructibus longo-stipitatis," for in the material at our disposal the perigynia were almost sessile; moreover the pistillate spikes were not always "*laxifloris*." But the most important characters derived from the structure of the perigynium "longo-conicis vel lanceolatis vix inflatis nervosis vel striatis" these were readily observed in the so-called *C. exsiccata*. *Carex mirata* belongs to a group of species, *Physocarpæ* Drej., in which a notable variation occurs in regard to the number, position, and length of the spikes, the staminate as well as the pistillate; also in regard to the structure of squama even in the same spike, not speaking of the orifice of the perigynium which, as Dewey has remarked himself, may vary from deeply cleft to merely bidentate. For this reason *C. mirata* Dew. may not be recognized without some difficulty, while, on the other hand, it would be utterly impossible to distinguish *C. exsiccata* Bail. except by means of specimens, since no diagnosis has been published.

Brookland, D. C., May, 1908.

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* This Journal (2), xxxix, p. 39, 1865.

Art. XLVI.—*Applications of the Lorentz-FitzGerald Hypothesis to Dynamical and Gravitational Problems;* by H. A. Bumstead.

There is at the present time a general consensus of opinion, among those best qualified to judge, that the fundamental facts of optics and electro-dynamics require us to assume that the ether does not partake (to any sensible extent) in the motion of material bodies which pass through it. The aberration of light is perhaps the most conspicuous of those phenomena which it has hitherto been found impossible to account for on any other hypothesis without becoming involved in serious difficulties.* All the phenomena in which there is relative motion of the source of light with respect to the observer, or of a material medium (through which light is propagated) with respect to source and observer, appear to require the above assumption, even those which at first seemed to lead to a conclusion somewhat different in form. Thus the experiment of Fizeau, in which he compared the velocities of light when going with, and against, a stream of water, was interpreted by Fresnel as indicating a certain entrainment of the ether. This interpretation was based on Fresnel's theory of refraction, which assumed that the etherial density was increased in material media; and it is only the excess ether which must be carried by the matter. On the electron theory, however (and indeed on any resonance theory of dispersion and refraction) there is no excess density of the ether in ponderable bodies; and it is not difficult to see that Fizeau's experiment requires a stationary ether.† A result which leads to the same view has been obtained in electro-dynamics by H. A. Wilson ‡ in measuring the electric force produced by moving an insulator in a magnetic field. All such experiments upon the effects of relative motion, so far as I know, give positive results which may be predicted from the hypothesis of a fixed ether, and the magnitude of the effects observed is in general of the same order as the fraction $\frac{v}{V}$, where v is the relative velocity involved, and V the velocity of light.

The theory of a stagnant ether leads us, however, in a no less direct manner to expect certain modifications in the phenomena of light and electricity when there is no relative motion of

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* Larmor, Aether and Matter, p. 37. Lorentz, Amst. Proc., p. 443, 1899; Abhandlungen, I, p. 454.

† See Lorentz, Versuch einer Theorie der Elektrischen und Optischen Erscheinungen, in Bewegten Körpern, § 68.

‡ Proc. Roy. Soc., lxxiii, p. 490, 1904.

material objects, but when all the apparatus concerned as well as the observer are carried through the ether with the velocity v. The effects to be expected are of the order of $\left(\frac{v}{V}\right)^2$; this is a very small fraction even when v is the velocity of the earth in its orbit, but the possible accuracy of certain optical experiments is so great that these effects could certainly be found if they existed without some compensating effect to mask them. As is well known, these effects have never been found; the first conclusively negative results were obtained in the celebrated experiments of Michelson and Morley,* and several other optical investigations have also failed to show the expected results. On the electrical side the problem has been attacked by Trouton and Noble,† who hung up an electrical condenser by a torsion wire and looked for a torque which, on the theory of a stagnant ether, ought to exist when the condenser is carried along by the earth. Although the sensitiveness of their experimental arrangement was ample for the observation of the expected second order effect, their result was also negative.

The most obvious interpretation of these results is that the ether near the earth has the same velocity as the earth; but, as has been stated, it appears to be impossible to reconcile this view with the great mass of optical and electro-dynamic evidence. The only satisfactory way out of this difficulty which has hitherto been suggested is a hypothesis put forward in 1892 by Lorentz,‡ and which had been independently suggested but not published by FitzGerald. According to this hypothesis, when any material body moves relatively to the ether its linear dimensions parallel to the direction of motion are contracted in the ratio of $\sqrt{1-\frac{v^2}{V^2}}$ to 1, while the dimensions perpendicular to the direction of motion remain unchanged. If this contraction takes place in the interferometer of Michelson and Morley and in the condenser of Trouton and Noble, their negative results are entirely explained on the theory of a stationary ether.§ As Lorentz points out, this contraction will be very small in any motions of material bodies which we can observe; for example the diameter of the earth in the direction of its orbital path will be diminished by only $6{\cdot}5^{\text{cm}}$ by its motion. It would moreover be impossible to detect the shrinkage, however great it might be, by ordinary

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* This Journal, xxxiv, p. 333, 1887.

† Phil. Trans. R. S. (A), ccii, p. 165, 1903.

‡ Versl. Akad. Wet. Amsterdam, 1892-3.

§ See Lorentz, Versuch einer Theorie, etc., § 89. Amsterdam Proceedings, 1903-4, p. 809, reprinted in Ions, Electrons, Corpuscules, vol. i, p. 477. See also Larmor in FitzGerald's Collected Papers, p. 566.

measurements, since the standards of length must shrink in the same ratio as the bodies to be measured.

It would be quite misleading, however, to leave the impression that this hypothesis depends for its credibility altogether upon the fact that it enables us to evade a serious difficulty and that it cannot be disproved by ordinary means. The electrical forces between charged bodies (electrons) are modified by motion through the ether; and they are modified in precisely such a way that if a given system of charges were in equilibrium under these forces in a certain configuration when at rest, it would when in motion be in equilibrium in a configuration obtained from the first by the application of the Lorentz-FitzGerald shrinkage. Now it is a fundamental theorem in electrostatics, that a charged system cannot be in equilibrium under the electrical forces alone; in the case of a collocation of electrons or atoms in equilibrium, the electrical forces must be balanced by other forces. If these inter-electronic forces are ethereal in origin and subject to the same laws as electro-magnetic forces, then the Lorentz-FitzGerald contraction would be expected *à priori;* and from this point of view the absence of the second order effects is evidence for the ethereal nature of inter-atomic and inter-molecular forces.

Forces of this character would suffice to account for the changed dimensions of moving bodies even if the electrons themselves were left unaltered by the motion. But, as Lorentz has pointed out,* we must also bring in dynamical considerations which show that for complete absence of second-order effects the electrons themselves must suffer the same contraction. The experiments of Lord Rayleigh† and of Brace‡ have shown that there is no double refraction due to the convection of transparent bodies by the earth. This implies that the periods of vibration of the electrons in the line of motion and perpendicular to it must be equal; and in order that this may be so, the longitudinal and the transverse masses of the electron must be altered by the motion in the same manner as the forces in these directions. An electron which does not change its shape (such as the rigid spherical electron of Abraham) will not have this property; nor will an electron which alters its form in any other manner than that described above for material bodies (such as the constant-volume electron of Bucherer). The electron proposed by Lorentz obviates these difficulties. If we assume that it is, when at rest, a sphere of radius, a, it must when in motion with velocity v, become an ellipsoid of revolution with its shorter axis in the direction of the motion and equal to $a\sqrt{1-\frac{v^2}{V^2}}$, the dimen-

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* Ions, Electrons, Corpuscules, vol. i, p. 477.

† Phil. Mag., vol. iv, p. 678, 1902.

‡ Phil. Mag., vol. vii, p. 317, 1904.

sions perpendicular to the motion remaining the same. If m_1 and m_2 are its longitudinal and transverse masses, and m_0 the mass for infinitesimal velocities, we shall have

$$m_1 = m_0 \frac{1}{(1-\beta^2)^{\frac{3}{2}}}$$

$$m_2 = m_0 \frac{1}{\sqrt{1-\beta^2}}$$

where, for brevity, β has been put for $\frac{v}{V}$. With this electron Lorentz has shown that no optical or electrical effects of motion through the ether can be detected.

The subject has been approached from a different standpoint, and treated in a very interesting and instructive manner by Einstein.* His fundamental postulate amounts to a denial that it is possible to observe any effects of uniform convection through the ether in which all the bodies concerned (including the observer) take part. This he calls the Principle of Relativity; the significance of the name is that only relative motion of one portion of matter with respect to another, or of one electrical charge with respect to another, can produce any observable effect; uniform motion, relative to the ether alone, becomes as impotent, if not as meaningless, as absolute motion.

Einstein considers two sets of coördinate axes, one at rest in the ether (x, y, z), while the other moves with the constant velocity v in the x direction (ξ, η, ζ). He defines carefully the meaning of "time" (t in the fixed system, τ in the moving system) by means of clocks distributed at various points, some at rest with the fixed axes, and some moving with the moving axes. The clocks are supposed to be synchronized by light signals. By kinematic considerations he shows that, in order for the principle of relativity to hold, we must have,

$$\xi = \frac{1}{\sqrt{1-\beta^2}}(x - vt)$$

$$\eta = y$$

$$\zeta = z$$

$$\tau = \frac{1}{\sqrt{1-\beta^2}}\left(t - \frac{v}{V^2}x\right)$$

where, as before, $\beta = \frac{v}{V}$.

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* Ann. d. Phys., xvii, p. 891, 1905.

The distances x, y, z are measured by standards at rest, ξ, η, ζ, by standards in motion. The distance between two points (say on the x-axis) when measured by the first is x_2-x_1; when measured by the second, it is $\xi_2-\xi_1=\frac{x_2-x_1}{\sqrt{1-\beta^2}}$. The length of the moving standards, when parallel to the axis of x are thus $\sqrt{1-\beta^2}$ times the fixed standards; when perpendicular to x, they have the same length as the fixed standards. In order therefore that Einstein's principle should hold, it is necessary that all moving objects should suffer the Lorentz-FitzGerald contraction.

It is easy to compare the rates of the fixed and moving clocks by considering two events whose difference in time as measured by the fixed clocks is t_2-t_1; as measured by a moving clock whese coördinate is ξ', let the interval be $\tau_2-\tau_1$. Then

$$\tau_2-\tau_1=\frac{1}{\sqrt{1-\beta^2}}\left[t_2-t_1-\frac{v}{V_2}(x_2-x_1)\right]$$

But $x_2=\sqrt{1-\beta^2}\,\xi'-vt_2$ and $x_1=\sqrt{1-\beta^2}\,\xi'-vt_1$

So that $\tau_2-\tau_1=\sqrt{1-\beta^2}\,(t_2-t_1)$.

Thus the moving clocks run slower than the fixed ones; if a clock at rest beats seconds, it must, when in motion, have a period of $\frac{1}{\sqrt{1-\beta^2}}$ seconds.*

It is possible that the principle of relativity may come to be regarded as one of the fundamental empirical laws of Physics, occupying a position analogous to that of the Second Law of Thermodynamics. It rests on a similar basis, in that no deviations from it have been observed. Indeed the analogy may be made more complete by showing that the denial of the principle leads to a third kind of perpetual motion, by which the kinetic energy of any body might be exhausted and the body be brought to rest with reference to the ether.† There is however an enormous difference in the breadth of the evidence on which the two principles rest. Violations of the principle of relativity lead only to minute effects which must be sought for in difficult and recondite experiments. The fact remains however that, so far as our knowledge extends, the principle holds; the most reasonable course in regard to it, and that which promises to be most fertile in results, is to accept it provisionally and to develop its conse-

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* This relation between the time in fixed and moving systems was also taken into account by Lorentz, by means of a variable which he calls local time. Versuch einer Theorie, § 31.

† Larmor in FitzGerald's Papers, p. 566.

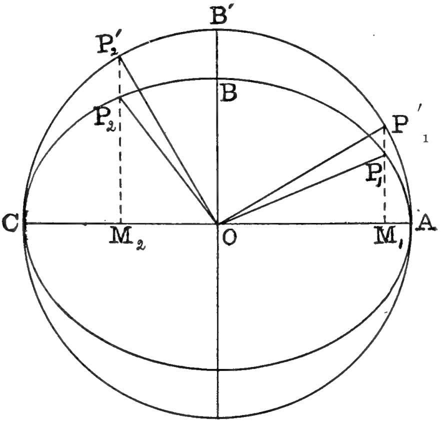
quences. This will doubtless lead to further experimental tests; and even apart from direct tests, one may regard the evidence for the principle as being strengthened if it introduces simplification and harmony into the theory of phenomena which are apparently remote from those that led originally to its adoption.

As the dimensions of all bodies are altered by motion through the ether, it is plain that such motion must be taken into account in the exact theory of even purely dynamical phenomena. As such applications are not very familiar and present some points of interest, it seems not altogether superfluous to consider a few very simple dynamical cases from this point of view.

The Torsion Pendulum.

Suppose a bar of length L (when at rest) hung up by a torsion wire in the ordinary way. Let the apparatus be carried by the earth through the ether with the velocity v in a direction perpendicular to the wire; and let us consider the period of the pendulum when the bar is clamped to the wire in two different positions: (1) with its length perpendicular to the earth's motion, and (2) parallel to the direction of motion. By the principle of relativity the two periods must be equal. As the length of the bar in the first position is L and in the second position $\sqrt{1-\beta^2}$ L, it appears at first sight that the mass of every particle of the bar should be greater in position (2) when it is moving perpendicularly to the earth's motion than in (1) when it is moving parallel to it. This would make the

FIG. 1.



transverse mass greater than the longitudinal, whereas the opposite is the case with the apparent mass due to electrical charges. A closer consideration however shows that this is an error arising from the application of the ideas of rigid dynamics to a body which is changing its shape.

The path of any particle of the bar, if measured by a scale carried along with the earth, will appear to be the circle AB′C; if measured with reference to a scale at rest however it will be the ellipse ABC in which $OB = \sqrt{1-\beta^2}\,OA$. For brevity we shall refer to these as the "apparent" and the "true" paths. In case (1), let P_1 be the true position of the particle, P_1' its apparent position; let $OM_1 = x_1$; $M_1P_1 = y_1$; $\measuredangle AOP_1 = \theta_1$; $\measuredangle AOP_1' = \theta_1'$. In case (2), let $OM_2 = x_2$; $M_2P_2 = y_2$; $\measuredangle BOP_2 = \theta_2$; $\measuredangle BOP_2' = \theta_2'$. The potential energy of the twisted wire in either case depends on the *apparent* angle θ_1' or θ_2'. This is seen if we consider two pointers attached to the wire, one along OA when the wire is untwisted and the other along OB; if the wire is now given any twist the two apparent angles θ_1' and θ_2' will be the same, but the real angles θ_1 and θ_2 will be different as well as the two elliptical arcs traced out by the ends of the pointers. As the apparent motion is isochronous we may put the potential energy equal to $\frac{1}{2}k\,\theta'^2$.

In position (1) we have

$$y_1 = x_1\sqrt{1-\beta^2}\tan\theta',$$

For small oscillations, $x_1 = a$; $\tan\theta'_1 = \theta'_1$ and

$$y_1 = a\sqrt{1-\beta^2}\,\theta'_1$$

Thus the potential energy is $\frac{1}{2}\,\frac{k}{a^2(1-\beta^2)}\,y_1^2$; the equation of motion of the particle becomes

$$m_1\ddot{y}_1 = -\frac{k}{a^2(1-\beta^2)}\,y_1$$

and the period of oscillation

$$T_1 = 2\pi\sqrt{\frac{m_1(1-\beta^2)\,a^2}{k}}$$

In case (2)

$x_2 = a\sin\theta'_2 = a\theta'_2$ for small oscillations. The potential energy is thus $\frac{1}{2}\,\frac{k}{a^2}\,x_2^2$, and the period

$$T_2 = 2\pi\sqrt{\frac{m_2a^2}{k}}$$

In order for these periods to be equal we must have

$$m_2 = (1 - \beta^2)\, m_1$$

which is the same relation as that between the longitudinal and transverse masses of Lorentz's electron. That the variation with the velocity of m_1 or m_2 for ordinary matter is also the same as for Lorentz's electron may be shown in many ways; the following simple example will suffice for the purpose.

Consider an elastic rod with its length perpendicular to the motion of the earth and making longitudinal vibrations. If its period of vibration is T we shall have

$$T \propto \sqrt{\frac{m_2}{\kappa}}$$

where m_2 is the transverse mass of any particle and κ is the coefficient of stretching of the rod. We must also have, by Einstein's transformation,

$$T = \frac{T_0}{\sqrt{1 - \beta^2}}$$

where T_0 is the period of the rod when at rest.*

The constant κ depends on the intermolecular forces in the direction of the length of the rod, that is perpendicular to the earth's motion; and these must vary with the velocity in the same manner as electrical forces. If we have two point charges moving through the ether in a direction perpendicular to the line joining them, the force between them is

$$E = E_0 \sqrt{1 - \beta^2}$$

where E_0 is the force when they are at rest.† Thus we have

$$\kappa = \kappa_0 \sqrt{1 - \beta^2}$$

and

$$\sqrt{\frac{m_2}{\kappa_0 \sqrt{1 - \beta^2}}} = \sqrt{\frac{m_0}{\kappa_0}}\, \frac{1}{\sqrt{1 - \beta^2}}$$

whence

$$m_2 = m_0 \frac{1}{\sqrt{1 - \beta^2}}$$

It follows therefore from our hypothesis not only that all mass is electromagnetic but also that it varies with the speed in the specific manner of Lorentz's electron.

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* If this relation did not hold for any time-keeper, the velocity of light measured in a moving system would be different from that measured in a system at rest, and thus the principle of relativity would be violated.

† See below, p. 503.

The Gravitational Pendulum.

As a further example, consider a simple pendulum at a point on the earth's surface 90° from the pole of its motion, so that the string is perpendicular to the direction of motion. When it vibrates in a plane at right angles to the motion the path of the bob is a circular arc and the period is

$$T = 2\pi \sqrt{\frac{m_2 L}{G}}$$

where G is the force with which the earth attracts the bob. When it vibrates in the plane of motion its path is the arc of an ellipse whose axes are L and $L\sqrt{1-\beta^2}$; for the same vertical height (that is for the same potential energy), the infinitesimal arc described will be in this case less than in the other in the ratio of $\sqrt{1-\beta^2}$ to unity. So that the period is

$$T = 2\pi \sqrt{\frac{m_1(1-\beta^2)L}{G}}$$

giving the same ratio of masses as before.

Comparing, say, the first of these with the period which the pendulum would have if the earth were at rest, we have

$$\sqrt{1-\beta^2}\sqrt{\frac{m_2 L}{G}} = \sqrt{\frac{m_0 L}{G_0}}$$

and since

$$m_2 = m_0 \frac{1}{\sqrt{1-\beta^2}},$$

$$G = \sqrt{1-\beta^2}\, G_0$$

Thus the gravitational force between two bodies moving at right angles to the line joining them is the same function of the velocity as the electric force between two moving charges in a corresponding position.*

If we imagine the pendulum suspended at the place on the earth which is foremost or rearmost in its motion, the length of the string will be $L\sqrt{1-\beta^2}$ and the period

$$T = 2\pi \sqrt{\frac{m_2 L\sqrt{1-\beta^2}}{G'}}$$

whence

$$G_1 = (1-\beta^2)\, G_0$$

which again corresponds to the electrical case when the line joining the charges is parallel to the motion.†

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* See p. 503.

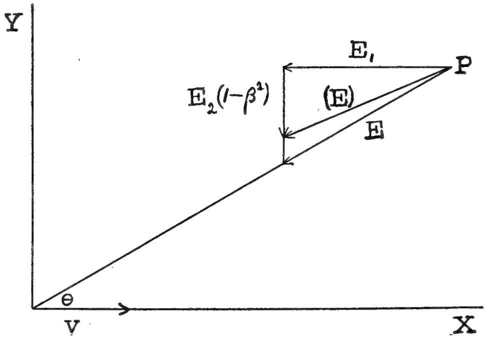
† See below p. 503.

It is scarcely necessary to point out that such problems as we have been considering do not lead to any practicable experimental tests. In order to detect deviations, it would be necessary to measure the periods in question with an accuracy such that the errors should be less than 10^{-8}, which is quite out of the question at present. This does not however affect the legitimacy of the use of such methods in following out the consequences of the principle; just as the impossibility of actually constructing a reversible engine does not invalidate that method of applying the second law of thermodynamics. More general methods might be used; but there is some advantage, especially in a comparatively new subject, in the simplicity and concreteness of ideas derived from the consideration of special problems.

Applications to Gravitation.

A promising direction in which to look for possible tests of the hypothesis is among the consequences of the deduction that gravitational forces must vary with motion through the ether in the same manner as electrical forces. If we have a point charge e moving alone the axis of x, with the uniform velocity v, the electric intensity at a point P whose coördinates are r, θ is

FIG. 2.



$$\mathbf{E}=\mathrm{V}^2\frac{e\,(1-\beta^2)}{r^2\,(1-\beta^2\sin^2\theta)^{\frac{3}{2}}}\,\mathbf{r}_1 \tag{1}$$

where $\mathbf{r}_1$ is a unit vector in the direction of r and $\beta=\frac{v}{\mathrm{V}}$.* The magnetic force is perpendicular to the plane of $\mathbf{r}$ and $\mathbf{v}$ and has the magnitude

$$\mathrm{H}=\frac{v}{\mathrm{V}^2}\,\mathrm{E}\sin\theta=\frac{ve\,(1-\beta^2)\sin\theta}{r^2\,(1-\beta^2\sin^2\theta)^{\frac{3}{2}}} \tag{2}$$

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* Electromagnetic units are used.

These are also the values of the electric and magnetic forces produced at points outside, by Lorentz's electron, or by any charged system in which, when at rest, the charge is distributed with spherical symmetry and which, when in motion, suffers the Lorentz-FitzGerald contraction. **E** is the force exerted by the moving charge e, upon a unit charge *which is at rest* at the point P. If the unit charge at P is in motion with the velocity **u**, then the force exerted upon it, which we may call (**E**), is

$$(\mathbf{E})=\mathbf{E}+\mathbf{u}\times\mathbf{H} \tag{3}$$

where $\mathbf{u}\times\mathbf{H}$ represents the vector product. Thus the force on a charge at rest at the point, P, is in the direction of r, but this is not true in general if it is in motion.

Let us consider first the special case when the two charges have the same velocity, $\mathbf{u}=\mathbf{v}$. Let the two components of **E** parallel and perpendicular to **v** be E_1 and E_2, respectively. The force $\mathbf{v}\times\mathbf{H}$ will be parallel to E_2 and in the opposite direction and its magnitude will be vH. So that the corresponding components of (**E**) are

$$(\mathrm{E})_1 = \mathrm{E}\cos\theta \tag{4}$$

and

$$(\mathrm{E})_2 = \mathrm{E}\sin\theta - v\mathrm{H}$$

or since

$$\mathrm{H} = \frac{v}{\mathrm{V}^2}\,\mathrm{E}\sin\theta,$$

$$(\mathrm{E})_2 = \mathrm{E}\sin\theta\,(1-\beta^2) \tag{5}$$

These are the components of the actual force on the moving charge at P; if it is of opposite sign to the charge e, the force will have the direction given in fig. 2.

When $\theta = 0$, $(\mathrm{E})_2 = 0$ and

$$(\mathrm{E})_1 = \mathrm{E} = \mathrm{V}^2\,\frac{e\,(1-\beta^2)}{r^2}$$

which is $(1-\beta^2)$ times the value of the electrostatic force when the charges are at rest: this corresponds to the gravitational case of p. 501 when the force was in the direction of motion.

When $\theta = \frac{\pi}{2}$, $(\mathrm{E})_1 = 0$, and

$$(\mathrm{E})_2 = \mathrm{E}\,(1-\beta^2) = \mathrm{V}^2\,\frac{e}{r^2}\,\sqrt{1-\beta^2}$$

which also agrees with the corresponding case for gravitation.

If we apply this electromagnetic law of force to gravitation we are at first sight confronted with the difficulty that the magnitude of the force varies not only with the distance but also with the angle θ; and there is also an aberration in the direction of the force. It is important, however, to notice that the variation and aberration of the force is of the second order in the small fraction $\frac{v}{V}$,* instead of the first order as has often been assumed in discussing the possible speed of propagation of gravitational force.†

In the special case before us, the principle of relativity relieves us entirely from the difficulty of even these small variations from the Newtonian law. This is apparent from the general statement of the principle; but it is of some interest to see how the matter works out in detail. What is subject to observation is not the force but the acceleration; if we let f_1 and f_2 be the components of the acceleration parallel and perpendicular to the common motion of the two bodies, we shall have

$$\left.\begin{aligned} f_1 &= \frac{(E)_1}{m_1} = \frac{(1-\beta^2)^{\frac{3}{2}}}{m_0} E \cos\theta \\ f_2 &= \frac{(E)_2}{m_2} = \frac{(1-\beta^2)^{\frac{1}{2}}}{m_0} E \sin\theta\,(1-\beta^2) \end{aligned}\right\} \qquad (6)$$

and the resultant of these is along r, so that there is no aberration of the acceleration. With regard to the variation of the acceleration with the distance, it must be remembered that, to an observer moving with the system, apparent distances in the direction of motion, (x), are greater than their true values in the ratio $\frac{1}{\sqrt{1-\beta^2}}$. Thus if the "true" coördinates of P (fig. 2) are x, y, the "apparent" coördinates will be x', y, where $x' = \frac{x}{\sqrt{1-\beta^2}}$. The "true" distance, r, will be the radius vector of an ellipse whose major axis is the "apparent" distance, r', and whose minor axis is $\sqrt{1-\beta^2}\, r'$; the polar equation of the ellipse (θ being measured from the minor axis) gives

$$\left.\begin{aligned} r^2 &= \frac{r'^2(1-\beta^2)}{1-\beta^2\sin^2\theta}; \\ x'^2 &+ y^2 = r'^2. \end{aligned}\right\} \qquad (7)$$

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* This was pointed out by Heaviside, who was the first, so far as I know, to apply the modern electrodynamics to gravitation. Electrician, 1893, July 14 and Aug. 4. Electromagnetic Theory, Vol. I, Appendix B.

† The general reason for this has been put very clearly by Lorentz, Amsterdam Proceedings, II, p. 573, 1900.

We must also observe that the "apparent" acceleration (f_1', f_2') differs from the "true" acceleration not only on account of the different scale of length in the x direction, but also because of the larger unit of time given by a moving clock. Thus

$$\left.\begin{aligned} f_1' &= \frac{1}{1-\beta^2} f_1 \frac{x'}{x} \\ f_2' &= \frac{1}{1-\beta^2} f_2 \end{aligned}\right\} \quad (8)$$

In equations (6) put $\frac{x}{r}$ for $\cos\theta$, and $\frac{y}{r}$ for $\sin\theta$; put for E its value from (1) and for r its value from (7); substituting in (8) the values thus obtained for f_1 and f_2, we obtain.

$$f_1' = \mathrm{V}^2 \frac{e}{r'^2} x'$$

$$f_2' = \mathrm{V}^2 \frac{e}{r'^2} y$$

The resultant "apparent" acceleration will thus be

$$\mathbf{f}' = \mathrm{V}^2 \frac{e}{r'^2} \mathbf{r}_1'$$

When $\mathbf{r}_1'$ is an "apparent" unit vector in the direction r'.

When there is *relative* motion of the planet with respect to the sun, however, the compensation is not perfect. In fact, deviations from the Newtonian law may be introduced which would not exist if the longitudinal and transverse masses were equal. This may be most easily seen when the attracting body is at rest in the ether with a planet moving about it; in this case the force given by electrical theory is the ordinary electrostatic force; it will be in the direction of the radius vector and will vary according to the inverse square of the distance. But the resultant acceleration will not be along the radius vector if the longitudinal and transverse masses are different. Let ϕ be the angle between the radius vector and the tangent to the path; and let the forces and accelerations, tangential and normal to the path, be respectively $\mathrm{F_t}$, $\mathrm{F_n}$, f_t, f_n. Then

$$\mathrm{F_t} = \mathrm{V}^2 \frac{e}{r^2} \cos\phi; \quad \mathrm{F_n} = \mathrm{V}^2 \frac{e}{r^2} \sin\phi$$

$$f_t = \frac{(1-\beta^2)^{\frac{3}{2}}}{m_0} \mathrm{F_t} = \frac{\mathrm{V}^2 e}{m_0 r^2} (1-\beta^2)^{\frac{3}{2}} \cos\phi$$

$$f_n = \frac{(1-\beta^2)^{\frac{1}{2}}}{m_0} \mathrm{F_n} = \frac{\mathrm{V}^2 e}{m_0 r^2} (1-\beta^2)^{\frac{1}{2}} \sin\phi$$

The acceleration along the radius vector is

$$f_n \sin\phi + f_t \cos\phi = \frac{V^2 e}{m_0 r^2}(1-\beta^2)^{\frac{1}{2}}(1-\beta^2\cos^2\phi)$$

The acceleration perpendicular to the radius vector is

$$f_n \cos\phi - f_t \sin\phi = \frac{V^2 e}{m_0 r^2}(1-\beta^2)^{\frac{1}{2}}\sin\phi\cos\phi\,.\,\beta^2$$

If we take the earth as a numerical example, this perpendicular acceleration is very small. Its maximum value will occur when the earth is at the extremities of the minor axis of its orbit; at this point

$$\cos\phi = \epsilon\,;\quad \sin\phi = \sqrt{1-\epsilon^2}\,;$$

where ϵ is the eccentricity of the orbit. Taking $\epsilon = 1{\cdot}7 \times 10^{-2}$ and $\beta^2 = 10^{-8}$ we find

$$\text{Acceleration along } r = \frac{V^2 e}{m_0 r^2}(1-\beta^2)^{\frac{1}{2}}\left[1 - 2{\cdot}9 \times 10^{-12}\right]$$

$$\text{Acceleration perpendicular to } r = \frac{V^2 e}{m_0 r^2}(1-\beta^2)^{\frac{1}{2}}\left[1{\cdot}7 \times 10^{-10}\right]$$

I am not sufficiently familiar with the details of astronomical calculations to be able to say with entire confidence whether or not such an acceleration perpendicular to r could be detected. It seems, however, unlikely. The maximum effect is of the same order as would be produced by a perturbing body at a distance equal to that of the sun, and whose mass was only $\frac{1}{200{,}000}$ that of the earth. The perturbation, moreover, would be periodic, vanishing at perihelion and aphelion and accelerating the earth's motion in one-half the orbit, retarding it in the other half.

When the sun is also moving, the problem becomes more complicated. For the present purpose it will be sufficient to obtain the order of magnitude of the acceleration perpendicular to the radius vector. Let $\mathbf{v}$ be the velocity of the sun, and $\mathbf{u}$ that of the planet *relative to the sun.* Then the force on the planet is

$$(\mathbf{E}) = \mathbf{E} + (\mathbf{v} + \mathbf{u}) \times \mathbf{H}$$

where $\mathbf{E}$ is given by equation (1), in which β is now the ratio of the velocity of the sun to the velocity of light, and θ is the angle between the radius vector and the sun's path. The magnitude of $\mathbf{H}$ is given by equation (2). The force $\mathbf{E}$ is along the radius vector; the force $(\mathbf{v} + \mathbf{u}) \times \mathbf{H}$ is normal to the resultant path of the planet. Let ψ be the angle between r and the tangent to the resultant path of the planet, then

$$F_t = E\cos\psi$$
$$F_n = E\sin\psi + |(\mathbf{v}+\mathbf{u})\times\mathbf{H}|$$

in which the term enclosed by vertical lines represents the magnitude only of the vector. **H** is perpendicular to the plane containing **r** and **v**; let u_1 be the component of **u** in this plane and let w be the resultant of u_1 and v. Then

$$|(\mathbf{v}+\mathbf{u})\times\mathbf{H}| = w\mathrm{H} = \frac{wv}{\mathrm{V}^2}\mathrm{E}\sin\theta$$

and
$$F_n = E\left(\sin\psi + \frac{wv}{\mathrm{V}^2}\sin\theta\right).$$

Dividing F_t and F_n by the longitudinal and transverse masses respectively, we obtain for the accelerations,

$$f_t = \frac{(1-\beta^2)^{\frac{3}{2}}}{m_0}\mathrm{E}\cos\psi$$

$$f_n = \frac{(1-\beta^2)^{\frac{1}{2}}}{m_0}\mathrm{E}\left(\sin\psi + \frac{wv}{\mathrm{V}^2}\sin\theta\right)$$

The acceleration perpendicular to the radius vector is

$$f_n\cos\psi - f_t\sin\psi = \frac{(1-\beta^2)^{\frac{1}{2}}}{m_0}\mathrm{E}\left(\beta^2\sin\psi\cos\psi + \frac{wv}{\mathrm{V}^2}\sin\theta\cos\psi\right).$$

Recent estimates make the sun's velocity about 20 kilometers per second, so that $\beta^2 = 0{\cdot}45\times10^{-8}$; its direction makes an angle with the plane of the earth's orbit of about 55°. When **r** is perpendicular to the plane containing **v** and the normal to the plane of the orbit, $\cos\psi$ is nearly zero; it must in fact be less than ϵ (the eccentricity of the orbit) even in the favorable case when the minor axis falls in this position; with the major axis in this position it will be zero. In this position, therefore, the acceleration perpendicular to the radius vector cannot be as much as twice that which was found for the sun at rest. When **r** is in the plane containing **v** and the normal to the plane of the orbit, $\theta = 55°$, $\psi < 55°$ and $w = v$. So that the acceleration perpendicular to the radius vector will be less than

$$\frac{(1-\beta^2)^{\frac{1}{2}}}{m_0}\mathrm{E}\,\beta^2\sin 110°$$

that is its ratio to the acceleration in the direction of the radius will be less than $1{\cdot}4\times10^{-9}$.

In order to be quite certain that astronomical facts are not in conflict with the principle of relativity, it will doubtless be necessary to make detailed comparisons between observation and calculation based upon this hypothesis. The small magnitude of the departures from the Newtonian law, of which more or less rough estimates have been given above, render it probable that there would be no serious lack of agreement. This probability is strengthened by a calculation published some years ago by Lorentz.* In this he found the secular variations of the elements of the orbit of Mercury due to the substitution of electro-dynamic forces for the strictly Newtonian force. The variations in the angular elements amounted to only a few seconds of arc in a century and the change in the eccentricity to 0·000005. He did not, it is true, take into account the effects of variable mass, which had not at that time become prominent even in electrical theory. The introduction of electromagnetic mass will, in general, tend to diminish the effects of the sun's motion and to exaggerate the effects of the motion of the earth relative to the sun. But from a comparison of the theoretical accelerations in the two cases, it does not appear that the variations could be increased enough to produce a sensible discrepancy.

[*Note added in Proof, Oct. 12.* Since the above was written, two papers have come to my knowledge which bear upon this question. A. Wilkens (Phys. Zeitschr., vii, p. 846, 1906) has introduced electromagnetic mass in the ordinary Newtonian equations and has calculated the resulting secular variations in the elements of Mercury, Venus, the Earth, Mars, and Encke's comet. In all cases the variations are within the limits of accuracy of the observations. F. Wacker (Ibid., p. 300) considers the case when both force and mass are electromagnetic and, upon applying his equations to Mercury, finds for the motion of its perihelion a value less than one-fifth of that which is at present unaccounted for. The changes in the scales of length and time which would be introduced by the principle of relativity could affect these results very little; so that it seems quite certain that our present observational knowledge of gravitation is not sufficiently exact either to exclude the general application of the principle or to supply evidence in its favor.]

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* Amsterdam Proc. II, p. 571, 1900.

SCIENTIFIC INTELLIGENCE.

I. CHEMISTRY AND PHYSICS.

1. *Utilization of Atmospheric Nitrogen.*—In a paper read before the Faraday Society, Dr. **ALBERT FRANK** has given an interesting account of recent progress in the preparation of nitrogen compounds from the nitrogen of the air, particularly in the form of calcium cyanamide, to which the commercial name nitrolim has been given. He discusses the production of Chili saltpeter and the approaching exhaustion of this source of nitrogen supply, and gives interesting data in regard to the production of ammonium sulphate in the gas industry. He indicates the increasing demand for nitrogenous compounds for agricultural fertilization, and shows that the synthetic products are assuming great importance. He states that the production of nitrates by the oxidation of atmospheric nitrogen is making excellent progress in Norway, but it is his opinion that the Norwegian saltpeter will remain the only direct competitor of the Chilian variety, on account of the cheapness with which electrical energy can be obtained in that country, which has unrivalled resources of water power. He states that calcium cyanamide has been found to be a satisfactory nitrogenous fertilizer, and gives an account of its preparation. The atmospheric nitrogen is first concentrated by the fractional distillation of liquid air by the Linde method. The remaining oxygen is then removed by passing the gas over heated metallic copper. The nitrogen is then absorbed by finely ground calcium carbide in a heated retort, according to the equation $CaC_2 + N_2 = CaCN_2 + C$. The product contains from 57 to 63 per cent of calcium cyanamide, giving about 20 to 22 per cent of nitrogen. The product is used directly as a fertilizer, and ammonia can be prepared from it very readily by the action of steam upon it. Works for the manufacture of this product have been started in many localities, most of which are in Europe, but one has been started on the Canadian side at Niagara Falls, and another in Japan. It is estimated that at the end of the present year works for the production of 45,000 tons of nitrogen by the cyanamide process will be in operation.—*Chem. News*, xcvii, 289 and 303.

H. L. W.

2. *The Action of Radium Emanation on Solutions of Copper Salts.*—Last year the sensational announcement was made by Ramsay and Cameron that they had observed the production of alkali metals, particularly lithium, in solutions of copper salts which had been subjected to the action of the radium emanation. These results appeared to be of so much importance that **MDME. CURIE** and **MDLLE. GLEDITSCH** have attempted to reproduce them. In the first place they placed a solution of copper salt in a little

glass flask into which a large quantity of emanation was introduced and allowed it to decay there spontaneously. In four such experiments lithium was detected in the solutions, while blank experiments in which no emanation was used gave no indications of lithium. The experiments were then repeated with every possible precaution. It was found to be extremely difficult to get chemical products free from lithium. It is present in distilled water, and almost all reagents; and if a reagent does not contain it, and is allowed to remain some time in a glass vessel, it is then found to contain traces of the element. Water which had been distilled from platinum and gave no test for lithium upon evaporation, gave a distinct spectroscopic test for that element after it had stood for 24 hours in a glass flask. It was found that fused quartz also contains lithium, and therefore platinum was selected as the material in which the careful experiments were carried out. As a result of these experiments the investigators were unable to find any indication of the production of lithium by the action of radium emanation upon solutions of copper salts, and therefore they could not confirm Ramsay and Cameron's results.—*Comptes, Rendus*, cxlvii, 345. H. L. W.

3. *The Formation of Mists in Presence of Radium Emanation.*—MDME. CURIE showed some time ago that the presence of radium emanation causes the condensation of saturant or nonsaturant water vapor as well as other vapors. This condensation is manifested by the formation of a persistent mist, visible by the light of an electric arc. Upon further study it is the author's opinion that chemical compounds capable of absorbing water vapor until drops are formed are produced under the action of the emanation. The mists are persistent and may last more than a month, and they disappear gradually as the emanation decays. With pure water and air charged with emanation, a slight mist lasting some days is observed. If the air is replaced by carbon dioxide, no persistent mist is observed. But if instead of pure water a mixture of equal weights of water and sulphuric acid is used, a dense, persistent mist is obtained. A very persistent mist is produced in the presence of concentrated sulphuric acid and carbon dioxide. It was found that a flask containing water and air charged with the emanation gave a much more dense mist when closed with a rubber stopper than when sealed up, and when a piece of sulphur was placed in the air in a similar sealed flask the amount of mist was increased, while traces of sulphuric acid could afterwards be detected in the water. Mists which were very intense at first and lasted more than a month were observed with petroleum ether and with carbon disulphide in the presence of air charged with emanation. Anhydrous ether in presence of carbon dioxide and the emanation also gave a persistent mist. Experiments with certain solids showed that in the presence of emanation, iodine and carbon dioxide as well as camphor and air gave dense mists of long duration. A mist may be observed with actinium in the presence of water and carbon

dioxide. The emanation must be fairly concentrated at first to produce the mist, which, however, may persist for a month when the concentration of the emanation has been reduced about 200 times.—*Comptes Rendus*, cxlvii, 379. H. L. W.

4. *The Preparation of Argon.*—FISCHER and RINGE have worked out a new method for producing argon from the air, which can be carried out on a relatively large scale at a moderate cost. The novel feature in the process consists in the use of calcium carbide for absorbing oxygen and nitrogen at a single step. This is used in the form of a powdered mixture of 90 per cent of calcium carbide and 10 per cent of calcium chloride heated in an iron vessel to 800° C. The absorption of these gases is complete after sufficient circulation, practically with the formation of calcium oxide, carbon, and calcium cyanamide, according to the equations $O_2 + 2CaC_2 = 2CaO + 4C$, and $N_2 + CaC_2 = CN_2Ca + C$. The authors prepared eleven liters of atmospheric argon in the course of two days by means of their apparatus, and showed its purity by making determinations of its density. They make the statements that the atmospheric air contains 0·937 per cent by volume of "noble gases," the so-called crude argon; that the density of crude argon is 19·94 compared with oxygen as 16; that crude argon itself consists of 99·75 per cent by volume of argon, and 0·25 per cent of a mixture of helium, neon, krypton, and xenon, in which neon with the density 10 predominates, so that crude argon is somewhat lighter than pure argon, the density of which is 19·95.—*Berichte*, xli, 2017. H. L. W.

5. *The Chemical Analysis of Iron;* by ANDREW A. BLAIR. Seventh edition. Pp. xix, 327, 108 figures and 5 tables. Philadelphia, 1908 (Lippincott & Co.).—This excellent handbook appears in its seventh edition, the first edition having been issued in 1888 (cf. (3), xxvi, 387). The fact that its admirable character has been fully recognized by those using it is well shown by the frequent revisions called for. The present edition contains a description of some new analytical processes concerning the separation of vanadium, molybdenum, chromium and nickel in steel; and further an account of the volumetric method for nickel. The methods for gas analysis have been revised, as also the subject of atomic weights; the table of factors for the latter have been recalculated from the values for 1908 given by the International Committee.

6. *Decomposition of Water Vapor by Electric Sparks.*—It has been suggested that the decomposition of water vapor in the case of thunderstorms may explain certain phenomena in those storms. Messrs. A. HOLT and E. HOPKINSON conclude from their experiments "that when electric sparks pass through water vapor or carbon dioxide the separation and arrangement of the decomposition products is not an electric phenomenon but results from gaseous diffusion. The hypothesis of electrolysis in liquids is therefore inapplicable."—*Phil. Mag.*, July, 1908, pp. 92–110.

J. T.

7. *Reflection from Glass at the Polarizing Angle.*—Lord RAYLEIGH concludes a study of this subject with the remark "that even a recently repolished surface, which may exhibit but a small ellipticity, is in a highly complicated condition. Grease itself may be comparatively inoperative optically on account of its index approximating to that of the glass. But why varying degrees of moisture should make so little difference is not apparent. Surface phenomena generally offer a wide field for investigation, which might lead to results throwing much needed light upon the constitution of matter."—*Phil. Mag.*, Sept., 1908, pp. 444–447. J. T.

8. *Emission of Electrons from Glowing Metallic Oxides.*—FELIX JENTZSCH refers to the work of J. J. Thomson and to that of Professor O. W. Richardson on the general subject of the emission of electrons from glowing bodies, and finds that the oxides arrange themselves in respect to rise in potential according to their electromotive series, that electropositive substances hold more free negative electrons than the electronegative. The work which the electron has to do in being thrown off is greater with electropositive substances. This work is performed only at the surface of the substances. The velocities of the electrons was found to be in agreement with Drude's theory and with the observation of Lenard on the photo effect. The paper of Jentzsch contains a comparison between the energy of electron emission and the radiation energy.—*Annalen der Physik*, No. 11, 1908, pp. 129–156. J. T.

9. *The Kinetic Energy of the Negative Electrons Emitted by Hot Bodies*—J. J. Thomson has stated that the carriers of negative electricity emitted by hot bodies are electrons. Prof. O. W. RICHARDSON has assumed that the transitional energy of the electrons inside the metal has the same value as that of the molecules of a gas at the same temperature as that of the metals, and that the translational kinetic energy of the electrons outside the metal possesses the same value. Professor Richardson's paper embodies the result of an investigation of the portion of the kinetic energy which depends upon the component of the velocity normal to the emitting surface. What is determined is the value of $\frac{1}{2}mu^2$ where m is the mass of an electron and u is its component of velocity perpendicular to the surface from which it is emitted.—*Phil. Mag.*, Sept., 1908, pp. 353–376. J. T.

II. GEOLOGY AND MINERALOGY.

1. *Die Entwicklung der Kontinente und ihrer Lebewelt, ein Beitrag zur Vergleichenden Erdgeschichte;* by THEODOR ARLDT. Pages 730, figures 17, and 23 maps. Leipzig, 1907 (Wilhelm Engelmann).—In this large and detailed work the Principal of the Realschule at Radeberg, Saxony, presents the history of continental development and their biota past and present.

So great an undertaking cannot be adequately reviewed here and the reader will be informed only as to the manner in which the study is presented. The first 30 pages summarize the methods of paleogeography according to petrographic, paleontologic, plant and animal data. Following these are 371 pages giving the biogeography of geologic organisms, a study of the greatest value to all desiring to know the regional and subregional distribution of extinct floras and faunas. A valuable feature of this part are the eight phylogenetic trees of the various classes of organisms and their geologic origin and duration. This is followed by 71 pages in regard to the ancient continents and oceans as Northatlantis, Angara, Gondwana, the Mediterranean and Antarctic regions. The Periodic Geological Appearances as glacial periods, eruptive periods, times of mountain-making, transgressions and cycles are discussed in 30 pages.

The third division of the book is historical (pp. 556-611) and treats of the paleogeography of the earth according to geologic systems, and is illustrated by ten paleogeographic maps. Most of these are reproductions of those in Frech's Lethæa, Lapparent's Traité, Neumayr's Erdgeschichte, and Koken's Vorwelt.

The book is a veritable storehouse of information and the three hundred and four sources from which it has been garnered are given on pp. 622-631. All is made readily accessible in indices of nearly one hundred pages arranged under authors, organisms (from classes to species), and locality-subject registers. C. S.

2. *Archhelenis und Archinotis;* by HERMANN VON IHERING. Pp. 350 and a paleogeographic map. Leipzig, 1907 (Wilhelm Engelmann).—The Director of the Museu Paulista, São Paulo, Brazil, has studied for many years the South American floras and faunas and their relationship with those of other land masses. In this book he brings together his more important papers published during the past thirty years and adds three new chapters. His hypotheses are based in the main on the distribution of the fresh-water faunas, especially the Unionidæ and Decapod crustacea, but he also considers the neotropical flora and the Tertiary marine faunas. Archiplata, embracing Chile and Argentina, has distinct biotic assemblages from those of Archibrazil or Archamazonia, i. e., Brazil south of the Amazon. The nature of the barrier separating these faunas remains undetermined, as he no longer holds to his former view that a sea flooded between them, keeping the wonderful Tertiary mammal fauna of Patagonia out of the northern region. Archiguiana refers to the lands north of the Amazon and has Antillean connections.

The southern half of Africa and Archiplata, united across the Atlantic, is his Archhelenis (practically Gondwana land of Suess). This vast land originates in Neumayr's Cretaceous Brazil-Ethiopian continent by breaking down in its northern Atlantic half during Cretaceous and in early Eocene time, the southern portion also passing beneath the sea in Oligocene time, establishing the present Atlantic ocean.

The great Mediterranean Thetis extended diagonally across Brazil between Archiguiana and Archamazonia to western Chili, spreading here its tropical marine fauna, which was prevented from also attaining California by the land mass Pacila. This very hypothetic land embraces the Antilles, Archiguiana, Central America, the Galapagos and west to the Hawaiian islands.

Archinotis is von Ihering's Antarctic continent of Mesozoic and Eocene time and embraces the Falkland Island, South Georgia across to South Australia connecting northward with this continent on one end and the other with Patagonia. It was greatly reduced polarward and its northern connections severed during Neogene time. C. S.

3. *Camarophorella, a Mississippian Meristelloid Brachiopod;* by JESSE E. HYDE. Proc. Boston Soc. Nat. Hist., 34, 1908, pp. 35–65, pls. 6–10.—This genus is shown not to belong in the Pentameridæ near Camarophoria but in an entirely different association, the Meristellinæ. The spiralia and the elevated muscular platforms are worked out in great detail and illustrated with excellent drawings. C. S.

4. *The Geology of Pike County;* by R. R. ROWLEY. Missouri Bureau of Geol. and Mines, VII, sec. ser., pp. 122, plates 6 and geological map.—Professor Rowley here brings together the results of his many years of work on the stratigraphy of Pike County, Missouri. The work is especially valuable for the detailed stratigraphy of the Paleozoic formations and the descriptions of the fossils on pages 56 to 101. C. S.

5. *Annual Report of the State Geologist of New Jersey, for the year 1907;* by HENRY B. KÜMMEL. Pp. ix, 192 with 50 plates. Trenton, 1908.—This volume contains an important report by H. B. Kümmel, C. C. Vermeule and L. M. Haupt, on the inland water-way from Cape May to Bay Head, accompanied by a series of folded maps; there is also a report on the improvement of Manasquan Inlet, by L. M. Haupt. Petrologists will be interested in the exhaustive paper on the Newark Igneous rocks of New Jersey, by J. Volney Lewis, pp. 97–167, accompanied by some forty excellent plates. An abstract by the author of a part of this important investigation was published in the August number of this Journal, pp. 155–162.

6. *Geological Survey of Canada.* R. W. BROCK, Acting Director. *General Index to Reports 1885–1906.* Compiled by F. J. NICOLAS. Pp. x, 1014. Ottawa, 1908 (Government Printing Bureau).—The New Series of Reports of the Canadian Geological Survey commenced in 1885 and extended to 1906; sixteen volumes in all have been published, some of them covering two years. The volnme now issued gives a complete Index to this long series and thus makes the large amount of important material contained readily accessible; this great labor has been well performed by Mr. F. J. Nicolas. The earlier index, prepared

by D. B. Dowling, covered the Survey's publications from 1863 to the end of the Old Series in 1884.

7. *Mission scientifique au Dahomey;* par H. HUBERT; 8°, 568 pp., 86 pls. and figs. and geol. map. Paris, 1908 (E. Larose).—This volume contains the results of two years of exploration in the Dahomey region of Africa, during which the principal subjects of study were the geological formations and the mineral resources of the colony. It is in fact, however, a detailed investigation of all the factors which determine the surface relief and climate of the area. The work was carried on under the auspices of the colonial government, aided by the French Association for the Advancement of Science.

After a general description of the topography and history of the country, the author presents the result of a study of its meteorology and then considers the action of exterior geological agencies in modifying its relief and the effects produced, notably the action of the atmosphere, of the surface waters, both from the chemical and mechanical sides, and of the sea. These detailed studies of an equatorial region contain many observations of interest and of value and the main geographical features of the country are now well determined.

The larger part of the volume is devoted to the areal geology. As a general result of his work the author finds that the rocks may be divided into three main series of undetermined age and these series cover each a remarkable extent of surface. The oldest consists of folded crystalline schists which form two great peneplains. The second are bedded rocks of unchanged altitude, which may be of early Paleozoic age, and the third are surficial deposits of recent formation. Unfortunately the lack of fossils prevents exact determination and correlation. A large area of deposits not far from the coast is thought to be of Eocene age. The folding of the first series is parallel and this has profoundly affected the evolution of the geography; the folds have determined the courses of the rivers, such as the windings, rapids, etc., of the Niger.

These rocks are cut by, or mingled with, eruptive masses in places, such as granites of various types, diorites, diabases and gabbros. Some of the gneisses are also recognized as of eruptive origin. The results of detailed microscopic study of these various rock types are also given, the most interesting being of certain alkalic granites containing riebeckite.

The last part of the work contains the results of the study of the distribution of certain plants and animals, that is of the biologic zones, and concludes with an ethnographic sketch of the region in which it is shown that the human grouping stands in close relation to certain features of geography.

The whole work is an important contribution to our knowledge of a very interesting country. L. V. P.

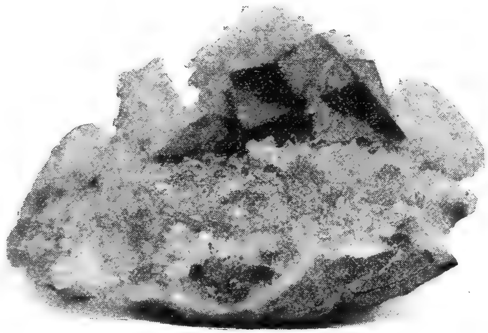
8. *The Fossil Turtles of North America*; by Oliver Perry Hay. Pp. 568, with 704 illustrations in text and 113 plates. Carnegie Institution of Washington, Publication No. 75, Washington, 1908.—All naturalists welcome this sumptuous volume on a subject that has too long remained in confusion by reason of a large number of imperfectly known forms and the even more serious lack of field work. Here, finally, the isolated facts are assembled and redescribed, and with many new discoveries, illustrated with a clearness and fulness that disarms all criticism. If one wished to see a few more references to European turtles, with the introduction of at least occasional comparative figures, the great size already reached by the volume would preclude fairness in such a wish. We do think, however, that omission from the legends of the source of adopted figures, and sometimes of plates, is not commendable. Fulness of legends affords one of the most effective aids in text condensation.

In completing his summary of the fossil turtles of North America, Dr. Hay finds 268 valid species, 76 of which are new. The Bridger Eocene has been particularly prolific in new forms, also the Laramie and Judith River Cretaceous; while the genus *Glyptops*, oldest of American forms, is found to include three new species and to extend into the uppermost Cretaceous. Our turtles culminated in size in the Fort Pierre, with also the greatest number of more or less distinctly salt-water forms; fresh-water forms were most numerous in the Bridger Eocene, and land forms at their largest in the late Tertiary. The presence of pleurodiran genera in the earlier faunæ is very interesting.

It is not clear why our pioneer collectors so persistently neglected the Testudinata, leaving nearly to accident until very recently the accumulation of adequate material for establishing the ancient history of this group. Highly modified, the most widely distributed of all the reptilian orders in both latitude and time, yet bound to be of stratigraphic value, and barely past their culmination in number and size, the turtles must, according to any fair hypothesis, finally yield a vast fund of information concerning evolutionary limits; they must, too, shed much light on problems of distribution. Their study, fortunately, is now set as far ahead as that of any other of the more extensive groups of fossil vertebrates yielded by this continent, if not indeed further. Dr. Hay's volume is, then, to say the least, epoch-making; for no comparable work on fossil turtles has appeared in Europe. And it is furthermore noteworthy from this symposium of American turtles, and especially from the large number of new forms added by Dr. Hay and others during the past ten years, augmenting previously known species by fully sixty per cent, that North America will eventually yield an enormous fossil turtle fauna. Particularly in the case of the more primitive forms and the Protostegidæ may we anticipate early results from exploration. The Carnegie Institution has thus opened to other workers a great field in which progress is now rendered rapid and accurate.

G. R. W.

8. *Beautiful Cinnabar Crystals from China;* by A. H. Petereit, New York (communicated).—In August last a small consignment of very interesting and beautiful cinnabar crystals was sent to the writer from China. They were found at Wanshanchang (Hamlet of Ten Thousand Hills) Tungyen Prefecture, Province of Kweichow. Cinnabar has been obtained before at two different localities in China, but not to compare in beauty and perfection with that illustrated here. These crystals are ordinary and interpenetrating twins of a bright ruby-red color; they are translucent, or in some cases transparent. The matrix is a pure white quartz, the crystals occurring in cavities with quartz crystals. The rare beauty of these crystals led the writer to urge his correspondent in China to scour the country for more and larger specimens. A second consignment of all that could be found has just arrived, and two of these remarkable specimens are shown in the figures, reproduced from photographs, actual size. It is stated that the mine from which these were taken is now filled with water, and will not again be worked.



III. BOTANY.

1. *Gray's New Manual of Botany. A Handbook of the Flowering Plants and Ferns of the Central and North-eastern United States and Canada.* Rearranged and extensively revised by BENJAMIN LINCOLN ROBINSON, Asa Gray Professor of Systematic Botany, and MERRITT LYNDON FERNALD, Assistant Professor of Botany, in Harvard University. Pp. 926. New York, 1908. (American Book Company.)—Sixty years have elapsed since the first edition of Gray's Manual of Botany was published. From time to time during that long period the treatise has received careful editorial attention, and necessary additions have been incorporated. Under the limitations of stereotyped pages, some of these additions have been, of course, rather unwelcome, and have found their place sometimes in supplementary pages of new issues. The last thorough revision before the present one was undertaken after Professor Gray's death. The work was very satisfactorily done by the late Dr. Sereno Watson and by Professor J. M. Coulter. Numerous important changes were made after the most careful deliberation, and the decisions proved acceptable to the majority of working botanists. But in the eighteen years which have passed since the publication of that sixth edition, great advances have been made all along the line in Systematic Botany, and it has been obvious that a new edition of the Manual is imperatively demanded. For some years this revision has been in progress at the Herbarium, where the first edition was prepared. The Curator of the Gray Herbarium, Professor Robinson, and his aid, Professor Fernald, have given to the task a great part of their time and the most loving care. Serious difficulties confronted them. In the first place, the accumulation of material of late has gone on with a rapidity which threatened to carry the size of the volume beyond the limits of convenience, so that it could not longer be called properly a "handbook." But by the exercise of much skill, the revisers have kept the book within reasonable bounds, and have given it essentially the form and size of the sixth edition. The second serious difficulty consisted in the absolute necessity of bringing order out of the chaotic condition of nomenclature. This order has been measurably secured by a consistent adherence to the Vienna agreement, which is justly acknowledged as International instead of provincial. But the synonyms which have found a place in other systems have here been placed within reach of the student. This part of the work has obviously demanded the exercise of the greatest care, and this it has received.

A third difficulty, promptly met, was the complete change, amounting almost to inversion, in the sequence of the natural families. This change has grown out of a recognition of affinities between plants, which compels a general re-arrangement. It is perhaps not too much to say that such a re-arrangement would have been unwise in 1890 when Drs. Watson and Coulter issued the sixth edition; it would manifestly have been unwise to fail to make this change to-day.

Many extremely perplexing questions of a minor character have been well and skilfully met by the authors of the present revision. One of these is the selection of illustrative helps. These are incorporated in the body of the page, and are not too numerous to be confusing. They are, for the most part, excellent and telling. Another difficulty, and the last to which we shall now refer, was the discrimination between forms in polymorphic genera where such differences can be made to appear as specific instead of varietal. The multiplying of these forms under the name of species has introduced a question of the first magnitude. Of course, one cannot expect to satisfy everybody even by compromises, but such compromises seem to be demanded now and then. The revisers, who may well be called the authors of the present edition of Gray's Manual, have shown great ability in managing these perplexing matters, and are to be congratulated on their success. G. L. G.

IV. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *Carnegie Institution of Washington.*—Recent publications of the Carnegie Institution are given in the following list (continued from p. 100):

No. 39. Handbook of Learned Societies and Institutions. America. Pp. viii, 592.

No. 75. The Fossil Turtles of North America; by OLIVER PERRY HAY. Pp. iv, 568, with 113 plates; 4to.

No. 85. (Massachusetts). Index of Economic Material in Documents of the States of the United States. Massachusetts, 1789-1904. Prepared for the Department of Economics and Sociology of the Carnegie Institution of Washington; by ADELAIDE R. HASSE. Pp. 310, 4to.

No. 87. Volume I, Parts I, II. The California Earthquake of April 18, 1906; by ANDREW C. LAWSON, chairman. In collaboration with G. K. GILBERT, H. F. REID, J. C. BRANNER, and others. Pp. xviii, 451, with 146 plates, 25 maps, 15 seismograms; 4to. Report of the State Earthquake Commission. In two volumes and Atlas.

No. 89. The Old Yellow Book. Source of Browning's The Ring and the Book, in complete photo-reproduction with translation, essay, and notes; by CHARLES W. HODELL. Pp. cclxii, 345, 4 plates.

No. 94. The Structure and Life History of the Hay-Scented Fern; by HENRY SHOEMAKER CONRAD. Pp. 56, with 25 plates.

No. 95. Papers of the Station for Experimental Evolutions, No. 10. Inheritance in Canaries; by CHARLES B. DAVENPORT. Pp. 26, 3 plates.

No. 99. Botanical Features of North American Deserts; by DANIEL TREMBLY MACDOUGAL. Pp. 111, 62 plates.

No. 101. The Variation and Correlations of certain Taxonomic Characters of Gryllus; by FRANK E. LUTZ. Pp. 63.

2. *Ricerche Lagunari;* in charge of G. P. MAGRINI, L. DE MARCHI, and T. GNESOTTO, under the auspices of the Reale Istituto Veneto di Scienze, Lettere ed Arti. *No. 8, Osservazioni Mareometriche, Lungo il litorale e in Laguna* (*Biennio 1906–1907*), 50 pp. and 3 figs. *No. 9, Impianti Mareografici Eseguiti*, 17 pp. and 4 photos. *No. 10, Operazioni Geodetiche Fondamentali per il Rilievo della Citta e Laguna di Venezia*, 64 pp., 2 photos, and 1 fig. Venice, 1908.—The reports of the study of the lagoons of Venice (see this Journal, xxi, 407, xxiii, 397, xxv, 89) are continued in the three bulletins listed above. The work has now advanced to the point where the velocity, direction of propagation, and physical character of the tidal wave are approximately determined. The records show also a rather uniform wave of translation and a second tide more or less undetermined. The stations of observation have been increased in number and some of them relocated until now there are three in the lagoon of Malamocco, ten in the lagoon of Venice, three in the lagoon of Chioggia, and one each in the lagoon of Murano and at Caorle.

Of especial assistance to the committee in charge of this investigation has been the action of the city of Venice in undertaking detailed geodetic work in the region about the city, including the establishing of a new base line. The plans include the preparation of a large scale topographical map of the entire district.

H. E. G.

3. *Beiträge zur Chemischen Physiologie und Pathologie*, herausgegeben von F. HOFMEISTER. XI Band. Braunschweig, 1908 (Fr. Vieweg und Sohn).—This volume concludes the independent existence of Hofmeister's *Beiträge*, which henceforth is to be merged with the *Biochemische Zeitschrift*, edited by Professor C. Neuberg of Berlin. Professor Hofmeister will enter the editorial board of the latter journal. The noteworthy contributions to physiology contained in the first ten volumes of the *Beiträge* have been referred to in these columns from year to year. The final volume forms no exception in point of merit. Among the forty or more papers mention may be made particularly of E. Friedmann's extensive studies of the katabolism of carboxylic acids in the animal body; Embden's investigations on the genesis of the acetone bodies; Wiechowski's observations on the formation of allantoïn in metabolism; Baer and Blum's experiments on acidosis; and, as usual, numerous contributions on proteins and their derivatives. L. B. M.

4. *Canada's Fertile Northland*; edited by ERNEST J. CHAMBERS. Pp. 139, with 6 tables and 5 maps in pocket. Ottawa, 1907 (Government Printing Bureau).—How extensive are the natural resources yet undeveloped in the vast northern area of the Dominion of Canada is well brought out in this volume. The information is given in the form of evidence presented to a Committee of the Senate by a considerable number of persons. This is classified as follows: the territory of Ungava; the region west of Hudson Bay; the navigability of Hudson Bay; the climate of Canada. A series of large maps accompany the report.

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SCIENTIFIC INTELLIGENCE.

VOL. XXVI. DECEMBER, 1908.

Established by BENJAMIN SILLIMAN in 1818.

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EDITOR: EDWARD S. DANA.

FOURTH SERIES

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1908

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THE

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[FOURTH SERIES.]

ART. XLVII.—*The Preparation of Urano-uranic Oxide*, U_3O_8, *and a Standard of Radio-activity;* by H. N. McCoy and G. C. Ashman.

It is obvious that for the comparison of the activities of radio-active substances a standard or unit of activity is of prime importance. One of us* has proposed to take as this unit the activity due to one square centimeter of a thick film of U_3O_8, of sufficient thickness to have maximum α-ray activity. It was shown that such a standard could be reproduced easily and apparently with quite definite activity. We have now studied the problem of the preparation of a standard of activity more fully, with the results recorded below.

The chief points of importance are:

First, The complete removal from uranium of radium and other active as well as inactive impurities;

Second, The preparation of an oxide of perfectly definite composition;

Third, The preparation of uniform films of the oxide.

Fourth, The activity due to the β rays.

Material from three distinct sources was used:

(A) So-called chemically pure uranyl nitrate from the firm of C. A. F. Kahlbaum. This was practically free from all ordinary impurities. The radium content, which was determined by means of the emanation, amounted to $2{\cdot}5 \times {\cdot}0^{-5}$ of the equilibrium quantity. A portion of this nitrate, recrystallized from water twice, constituted sample A. It was not tested for radium again, as the original amount would increase the activity less than 0·01 per cent.

(B) An old sample of uranyl acetate, which contained a considerable amount of sodium as the chief impurity. The amount

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* McCoy, Phil. Mag., xi, 177, 1906.

of radium present was very small: 2×10^{-6} of the equilibrium quantity. After conversion into nitrate and two crystallizations of the latter from water, no trace of impurity could be found by chemical tests; the material formed sample B.

(C) The third sample was prepared from the uranium extracted from 29 g. of pitchblende from the Wood Mine, Colorado and purified as previously described, (*loc. cit.*) The process in brief consisted in treating the nitric acid solution of the mineral, after removal of silica, with an excess of ammonium carbonate solution to remove iron, etc., and the filtrate with ammonium sulphide to remove copper, lead, etc. The crude uranyl carbonate, obtained by boiling the last filtrate, contained two per cent of the equilibrium quantity of radium. This was removed by three precipitations of barium sulphate in the solution, the first precipitate taking out 95 per cent of the radium then present. The U_3O_8 made from this material three years ago seemed to be very pure and had, as then stated, an activity within 0·15 per cent of that of another sample of U_3O_8, which was supposed to be, and probably was, of great purity. A large portion of this material had been kept in solution as ammonium uranyl carbonate from May, 1905 to November, 1907. During this time a very small precipitate had formed. The filtrate from this precipitate was boiled; the uranyl carbonate so formed was called sample C.

By decomposing uranyl nitrate at a temperature below redness, the orange oxide, UO_3, is obtained; this loses oxygen at a higher temperature, giving U_3O_8. This latter oxide is not perfectly stable, but loses oxygen slowly when *very* strongly heated, as first observed by Zimmerman.*

From considerations based upon the phase-rule, for the three-phase system, U_3O_8, UO_2 and O_2, the partial pressure of the oxygen is a function of the temperature; consequently for a fixed pressure of oxygen (say that in the atmosphere) there must be a definite temperature at which the three phases can exist in equilibrium; above this temperature U_3O_8 will pass into UO_2; below it, the dissociation will not take place. Since the temperature of a solid contained in a crucible heated in the flame of a blast-lamp is far from uniform throughout the mass, we have used an electric muffle which gave perfectly definite temperatures, which were accurately measured by means of a platinum-rhodium pyrometer.

In one experiment 7 g. of sample A, purified uranyl nitrate, was converted at a moderate temperature into the orange-colored trioxide. This was placed in a platinum crucible and heated in the electric muffle. The crucible was loosely covered, allowing free access of air. After constant weight had been

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* Ann. ccxxxii, 276, 1885.

TABLE I.

Duration of Heating.	Temperature.	Weight of Oxide.
60 min.	560° C.	3·698
35	600	3·697
75	600 to 700	3·693
Reduced to UO_2 in hydrogen, over Bunsen flame		(3·554)
The dioxide was reheated, in air, in the muffle.		
30	700°	3·691
And reduced to UO_2, as before		(3·552)
and again heated in the air, in the muffle:		
30	570°	3·690

This experiment was repeated several times with perfectly similar results.

reached, the U_3O_8 was reduced to UO_2 by the usual analytical method, heating over a Bunsen flame in a stream of hydrogen. The reduced oxide was again heated in air in the muffle. It absorbed oxygen rapidly and changed to U_3O_8. Table I gives the details of the experiment.

The reduction of an oxide of uranium to UO_2 and weighing in that form is a standard analytical method. Therefore the composition of the product obtained by the reduction may be considered as known. The mean weight of the UO_2, 3·553 g., corresponds to 3·693 g. of U_3O_8. The fact that the product formed in air at 700° has the same composition whether formed by the decomposition of the trioxide or by the oxidation of the dioxide shows that this temperature is below that at which the U_3O_8 can lose oxygen in contact with the air. There is, therefore, no danger that heating for any length of time will decompose U_3O_8 at 700°.

Nine portions of U_3O_8 were prepared from samples A, B and C, and made into ten standard films. Films nine and ten were made from the oxide prepared from sample A as shown in Table I. The U_3O_8 for film thirteen was made as follows: A portion of sample C was heated in the muffle, in air, for thirty minutes at 700°; weight 1·2134 g. This was then reduced by hydrogen and again heated in the muffle, in air, for thirty minutes, at 700°; weight 1·2133 g. Each of the remaining seven portions of U_3O_8 was prepared separately by heating the corresponding sample for forty to sixty minutes, in air, in the electric muffle, at 700°.

The method of preparation of films for activity measurements has previously been described in detail.* Seven films, Nos. 9 to 19 inclusive, were made in circular tin dishes $7·15^{cm}$ in diameter, with rims $0·8^{cm}$ high; films 23, 24 and 25 were made on flat copper plates, $7·00^{cm}$ in diameter.

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* McCoy, J. Amer. Chem. Soc., xxvii, 391, 1905; Phil. Mag., xi, 176, 1906; McCoy and Ross, J. Amer. Chem. Soc., xxix, 1698, 1907.

The activity measurements were made in a gold-leaf electroscope having an ionization chamber 19·5^{cm} square and a distance of 8·5^{cm} between the film and the electrode of the gold-leaf system. The scale of the micromoter microscope corresponded to potentials between 576 and 473 volts, the fall of potential across the scale being 103 volts. Our standard films, which had about 0·020 g. of oxide per sq. cm., were all sufficiently thick to have the maximum α-ray activity. The β-ray activity was small, but varied with the weight of the film. It was also evident from the nature of the β-rays that the observed activity of the latter must depend upon the size of the ionization chamber, which in the case of our electroscope, though large enough to get the maximum effect of the α-rays, was insufficient for the β-rays. We have determined the β-ray activity *for our electroscope* in the following manner: The standard films of U_3O_8 were covered with one to four pieces of aluminum foil 0·0043^{cm} thick and the resulting β-ray activity measured. The first layer of foil cut off all the α-rays and a portion of the β-rays. By graphical extrapolation of the curve having β-ray activity and number of foils as coördinates, it was found that this portion amounts to 9·2 per cent of the effective β-ray activity of the uncovered film.

The further data for the films made from samples A, B, and C are given in Table II, the activity being expressed in terms of an arbitrary unit.

TABLE II.

Films in tin dishes 7·15^{cm} in diameter with rims 0·8^{cm} high.

Sample	No.	Weight	α and β Activity	β Activity*	α Activity
A	9	0·816	1·0080	0·0108	0·9972
A	10	0·807	1·0075	0·0100	0·9975
B	18	0·820	0·9990	0·0020	0·9970
B	19	0·753	1·0005	0·0020	0·9985
C	13	0·920	1·0040	0·0110	0·9930
C	14	0·892	1·0010	0·0110	0·9900
C	15	0·793	1·0070	0·0154	0·9916
Films on flat copper plates 7·00^{cm} in diameter.					
A	23	0·694	1·1111	0·0296	1·0815
A	25	0·625	1·1080	0·0262	1·0818
B	24	0·629	1·0950	0·0133	1·0817

These results show that the method of making U_3O_8 gives a product of definite activity. The somewhat low activity of

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* The activities were measured before the maximum amounts of UX, which had been largely removed in the process of purification, had again accumulated; for this reason the β-ray activity of a film is not a definite function of its weight.

sample C may be due to a trace of impurity; but the value is sufficiently close to the mean for A and B to show that the method is satisfactory.

We next made a new set of films on flat copper plates which were cut on a lathe and were almost perfectly circular. These plates differed slightly in size, however, for which reason the diameter of each plate was measured (in two or more directions) with a comparator, capable of giving results accurate to 0·001^{cm}. The U_3O_8 for these films was prepared in a single portion from sample A. On account of the large quantity of material used it was necessary to continue the heating at 700° for about three hours in order to obtain constant weight. The activities are shown in Table III; the last column gives the corrected activity for exactly 7^{cm} diameter.

TABLE III.

No.	Weight	$\alpha+\beta$ Activity	β Activity	α Activity	Diameter	Corrected α Activity
30	0·6812	1·0800	0·0263	1·0537	7·0168	1·0487
28*a*	0·8776	1·0788	0·0347	1·0441	6·9912	1·0467
29*a*	0·7996	1·0861	0·0300	1·0561	7·0174	1·0509
29*b*	0·7770	1·0812	0·0288	1·0524	7·0174	1·0472
31*a*	0·7801	1·0935	0·0326	1·0609	7·0301	1·0519
33	0·7070	1·0737	0·0270	1·0467	6·9969	1·0476
34	0·7677	1·0796	0·0321	1·0475	6·9948	1·0491
34*a*	0·9107	1·0891	0·0364	1·0527	6·9948	1·0543
					Mean,	1·0495

The activities in Table III are also expressed in terms of an arbitrary unit, about three per cent greater than the unit used for Table II. One of us (*loc. cit.*) has proposed to take as the unit of radio-activity, the activity due to one sq. cm. of such films of U_3O_8 as those to which Table III refers. In terms of such a unit, the activity of each film of Table III is represented by its area.

Several years ago, Rutherford and McClung* determined the ionization current of layers of U_3O_8 of different thickness, when placed between parallel plates sufficiently far apart for the complete absorption of all the α-rays in the air between the plates. The saturation current per sq. cm. of surface was $4·0\times10^{-13}$ampere, for a weight of 0·0189 g. of U_3O_8 per sq. cm. This weight is great enough to give the maximum α-ray activity provided the material is in the form of a perfectly uniform film; but this was not the case in Rutherford and McClung's experiment, as the oxide was merely "dusted" on the plate and therefore the observed current was far below that for a

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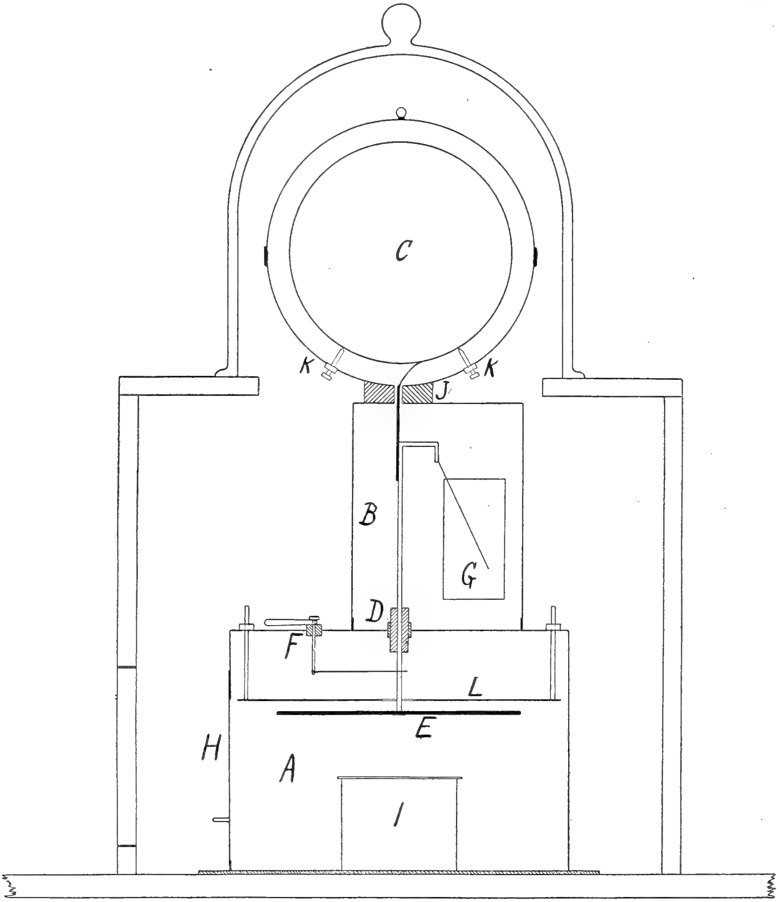
* Phil. Trans. A., cxcvi, 52, 1901.

perfectly uniform film.* We have made a determination of the saturation current in absolute units for the *a* radiation of our standard of activity. To do this we made use of a standard condenser of the concentric spheres type, in conjunction with a gold-leaf electroscope. See fig. 1.

FIG. 1.



The electroscope case consists of two rectangular compartments, made of sheet brass 1·5^{mm} thick. The ionization chamber, A, is 19·5^{cm} square and 14^{cm} high; the gold-leaf chamber B is 8 by 10^{cm} and 12·7^{cm} high. The gold-leaf system is insulated by an amber plug, D, and carries as its lower end the circular electrode, E, a brass plate 14^{cm} in diameter. F is

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* McCoy, J. Amer. Chem. Soc., xxvii, 395, 1905.

the charging device, which is connected with a three-point key, that keeps F earthed, except at the moment of charging. G represents a pair of glass windows, through which the motion of the leaf is observed by means of a micrometer microscope. The door, which slides upward, is at H. I is a metallic support of variable height, for the film. L is a flat metal plate 18^{cm} square with a 2^{cm} hole in the center; it is supported by a pair of brass rods at two diagonal corners and may be raised or lowered. When this plate, L, is placed about 3^{mm} above the electrode, E, the electrostatic capacity of the electroscope (without the condenser, C), is about five times as great as it is without L.*

The standard capacity, C, consists of two concentric spheres of sheet zinc.† The outer one is soldered to a brass block, J. having a 5^{mm} hole, through which passes a 1^{mm} brass wire soldered to the gold-leaf support; a very fine wire of spring brass makes contact with the inner sphere. The latter is supported by three amber pins, KK; each pin is threaded into a small brass ring, so as to be adjustable; the brass ring is carried by another ring of vulcanite, which insulates it from the sphere and enables the brass ring to be used as a guard ring. It was found, however, that the insulation was sufficiently good without the use of the guard rings. The upper half of the outer sphere is detachable; this arrangement allows the inner sphere to be introduced or removed readily. The whole apparatus is surrounded by a wooden case, surmounted by a glass bell-jar. This serves to keep the temperature uniform inside the gold-leaf chamber and so avoids air currents which greatly diminish the accuracy of the activity measurements.

The condenser spheres were made of spun sheet zinc. The radii were calculated from the weight of water required to fill each and the weight of the zinc of the smaller sphere. The exterior radius of the smaller sphere was $6{\cdot}293^{cm}$; the interior radius of the larger $7{\cdot}590^{cm}$. The capacity of the condenser

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* We have found that the observed activity of a given film is much more nearly constant when the capacity of the electroscope is increased by means of the plate, L; the reason for this is doubtless two-fold. First, the much slower movement of the leaf permits greater accuracy in timing; and second, the natural variation in activity during a fixed interval is a smaller fraction of the whole activity, the longer the interval. By increasing the time of discharge five-fold, the fractional error due to natural variation of activity would be reduced to less than half that for the more rapid discharge. See Geiger, Phil. Mag., xv, 539, 1908, and Meyer and Regener, Ann. Phys., xxiv, 757, 1908.

† The mode of combination of electroscope and condenser is a modification of that suggested by Prof. Millikan; Electricity, Sound and Light, p. 351, Ginn & Co. 1907.

was, therefore, $\frac{7{\cdot}590 \times 6{\cdot}293}{7{\cdot}590 - 6{\cdot}293} = 36{\cdot}83$ E.S.U. It is considered that when the inner sphere of the condenser is placed in position the calculated capacity, 38·83 E.S.U., is added to that of the system when this sphere is absent, but all else arranged as shown in the figure. Calling the capacity of the electroscope alone c_1 and with the condenser c_2, then the ionization current $i = \frac{p_1 c_1}{t_1} = \frac{p_2 c_2}{t_2}$ where p_1 and p_2 are the potential differences corresponding to the two ends of the scale and t_1 and t_2 are the times of discharge for the same film for the changes of potential p_1 and p_2 respectively. Therefore

$$c_1 = \frac{(c_2 - c_1)\, t_1 p_2}{t_2 p_1 - t_1 p_2}$$

The quantity $c_2 - c_1$ is the capacity of the condenser $= 36{\cdot}83$ E.S.U.

We used film No. 30, Table 3, placed at a distance of $3{\cdot}6^{\mathrm{cm}}$ below the electrode of the gold-leaf system. Experiment showed that this distance was entirely sufficient for the production of the maximum ionization current; at a distance of $4{\cdot}5^{\mathrm{cm}}$ or more the current was slightly smaller, owing, of course, to partial recombination of the ions.

As the closely agreeing means of several determinations, the times of discharge of the electroscope with and without the condenser were 243·9 and 420·9 sec. respectively, for the uncovered film. The times when the α-rays and 9·2 per cent of the β-rays were cut off by a sheet of aluminium $0{\cdot}0043^{\mathrm{cm}}$ thick were 10,860 and 12,435 sec. respectively.* From these data it follows that the times of discharge for the α-rays alone were 249·9 and 436·4 sec. respectively. The fall of potential across the scale was 103·05 volts without the capacity and 102·63 volts with the capacity, the measurements being made with an electrostatic voltmeter. From these data it is found that $c_1 = 48{\cdot}84$ E.S.U. and $c_2 = 36{\cdot}83 + 48{\cdot}84 = 85{\cdot}67$ E.S.U. Therefore the α-ray ionization current $i = \frac{p_1 c_1}{9 \times 10^{11} t_1} = 2{\cdot}238 \times 10^{-11}$ amp. Film No. 30 is $7{\cdot}0168^{\mathrm{cm}}$ in diameter; its area $= 38{\cdot}67$ sq. cm. Therefore the current per sq. cm. $= 5{\cdot}79 \times 10^{-13}$ amp. The total activity of 1 g. of uranium† is equal to that of 796 sq. cm. of a thick film of U_3O_8. Therefore the total α-ray ionization current of 1 g. of uranium $= 4{\cdot}61 \times 10^{-10}$ amp.

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* These times represent the 90·8 per cent of the β-ray leak plus the natural air leak and the leak across the insulation. The latter is somewhat greater when the condenser is attached to the electroscope; this makes the time 12,435 sec. shorter than would otherwise be expected.

† McCoy and Ross, *loc. cit.*

It is well known that the potential gradient required to produce a saturation current increases with increasing activity, the recombination of the ions being greater for a given potential gradient the more intense the ionization. It was, therefore, possible that the observed current for a standard film was below the maximum on this account. We made the following experiment to throw light on this point. Films of U_3O_8 were made in the usual way on a pair of semi-circular plates, made by cutting an ordinary 7^{cm} plate into halves. The activity of each half-film was measured separately and compared with that observed when the two were placed side by side to make a circular film. The sum of the separate activities was 0·33 per cent greater than that of the two together. The experimental error of the activity measurements did not exceed 0·05 per cent. The experiment shows that appreciably greater recombination of the ions takes place when the two plates act simultaneously, due to the more intense ionization. It follows from this, that the ionization current calculated above for one sq. cm. of U_3O_8 is somewhat smaller than that which actually would be observed for a film of unit area. However, the error which thus arises is eliminated in the calculation of the ionization current of unit mass of uranium or thorium; since in such a case the specific activity is calculated from the value based on the activity of an infinitely thin film* which would produce a vanishingly small ionic concentration. Consequently the ions would suffer no recombination and therefore the calculated ionization current is that which would be produced by all of the ions formed.

Boltwood† has determined the relative activity of radium and uranium by direct comparison of the activity of a minute known quantity of radium with the activity of very thin films of known weight of U_3O_8. It was found that radium (free from its products) is $1·30 \times 10^6$ times as active as an equal weight of uranium. Rutherford‡ found that the ionization current of a thin film of 0·484 mg. of pure $RaBr_2$, free from its active products, was $8·4 \times 10^{-8}$ amp. as measured by a sensitive galvanometer. Considering half of the α-rays to have been absorbed by the plate carrying the film, this is equivalent to a current of $5·94 \times 10^{-4}$ amp. for 1 g. of pure radium. We have found the total ionization current of 1 g. of uranium to be $4·61 \times 10^{-10}$ amp. Therefore the α-ray activity of radium (free from its products) is $1·29 \times 10^6$ times that of an equal weight of uranium, a result which is in good agreement with that found by Boltwood.

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* McCoy, Jour. Amer. Chem. Soc., xxvii, 402, 1905.

† This Journal, xxv, p. 296, 1908.

‡ Phil. Mag., x, p. 207, 1905.

Summary.

1. Uranium is easily freed from all other radio-active substances.

2. Pure U_3O_8 of perfectly definite composition is readily obtained by heating any lower or higher oxide of uranium in air at 700°

3. Uniform films of U_3O_8, 7^{cm} in diameter, weighing 0·6 to 0·8 g., have definite and constant α-ray activity and are therefore recommended as *standards of radio-activity.*

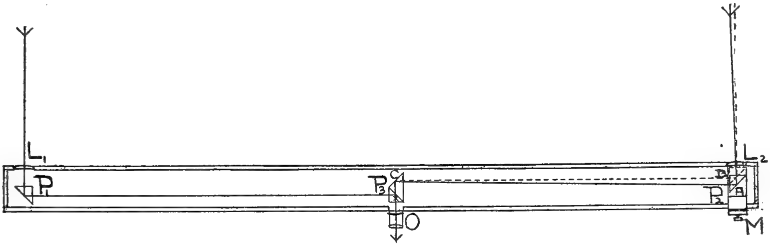
4. The α-ray saturation current for such a standard film was measured in absolute units and from the results the total ionization current for 1 g. of uranium, in an infinitely thin film, was calculated.

Kent Chemical Laboratory, University of Chicago, Sept., 1908.

ART. XLVIII.—*A Telemeter with Micrometer Screw Adjustment;* by FRED. EUGENE WRIGHT.

DURING the past few years many different devices have been suggested for measuring the distance to a distant object by merely sighting at it, and some of these, particularly the stereocomparator of Pulfrich, have proved serviceable. Three or four years ago, in connection with geological field work involving considerable topographic sketching, the need of such an instrument was keenly felt by the writer and the following apparatus devised. The apparatus is simple in construction and sufficiently accurate for the purposes for which it is intended. It appears, moreover, to be constructed on a principle not heretofore applied to telemeters, and may, therefore, be described very briefly.

FIG. 1.



The principle of its construction* is illustrated in fig. 1. Light waves from a distant object strike the two telescopic lenses L_1 and L_2 (both 50^{cm} focus) and after transmission are reflected from the two right-angled prisms P_1 and P_2 to the reflecting prism pair P_3, and thence to the ocular O. The incident rays are not precisely parallel and do not converge to the same point in the focal plane of the ocular. They can be made to do so, however, by moving the prism P_2 back parallel with itself by means of the micrometer screw M until the two points coincide and merge apparently into one (indicated by the cross in front of the ocular). The angle between the incident light rays from objects at different distances is different, but by moving the micrometer screw the two images resulting therefrom can be brought to coincidence.

Conversely, having once calibrated the micrometer screw readings for a number of distances, it is not difficult to inter-

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* The two test telemeters which have thus far been constructed on this principle were made in the workshop of the Geophysical Laboratory and can be duplicated by any good maker of instruments.

polate and to draw a curve indicating the distance away of any object in terms of micrometer screw readings. The equation expressing the relation between micrometer screw readings and distances away of objects is derived below (page 534).

The optical parts of the instrument are the following: Two achromatic plano-convex telescopic lenses, 50^{cm} focal length and 25^{mm} diameter; two right angle reflecting prisms P_1 and P_2, 18^{mm} length of side; a reflecting prism pair P_3 consisting of two right-angled reflecting prisms, the larger one of 20^{mm} edge and the smaller one of 14^{mm} edge, its hypothenuse face fitting the side of the larger prism closely. The hypothenuse surface of this smaller prism is silvered; at its center, a round circular portion 3 to 5^{mm} in diameter has been removed as in the Abbé camera lucida reflecting prisms. The two prisms are cemented with Canada balsam, the light from the larger prism reaching the ocular through the central part of the field, while that from the smaller prism is reflected by the peripheral silvered margin.

FIG. 2*a*.

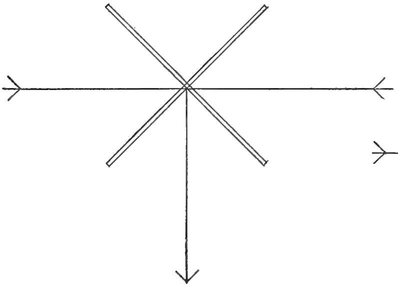
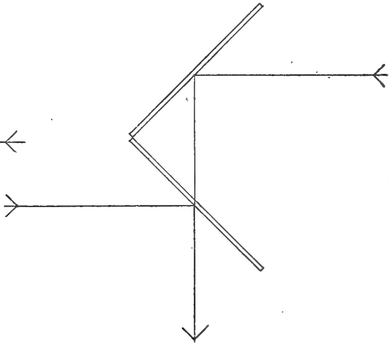


FIG. 2*b*.



Experiments with this type of double reflecting prism have indicated that the instrument should be so built that for average distances the round aperture in the center of the field should be situated near the focal plane of the ocular O.

Other reflecting devices were tried in place of the prism pair P_3, two of which are shown in figs. 2*a* and 2*b*, in which plane parallel glass plates are used. The four glass plates of fig. 2*a* are very difficult to adjust accurately and for the purpose special adjustment facilities had to be constructed. The device of fig. 2*b* consists of two glass plates and the light rays follow the paths indicated by the arrowed lines. With the glass plate devices the images are superimposed, while with the prism pair P_3 the image in the central part of the field forms the continuation of that in the margin. By placing the reflecting prism, however, so that it is at some distance from the focal plane of the ocular, the two reflected images can likewise be superimposed. This was done on a trial test by replacing in fig. 3 the prism P_3 by a total prism pair, thus bringing the light from both L_1 and L_2 to a common path and to reflection in a single reflecting prism at P_4 in place of the prism pair there indicated. The unfavorable features of the glass plate reflecting devices are chiefly the great loss of light and consequent dim field, and the double image from each lens which results from reflection from the two sides of each glass plate. For these reasons the permanent use of glass plates in this connection hardly seems feasible. Several other reflecting prism devices were tried, but that of fig. 1 and its modification in fig. 3 have thus far proved most satisfactory.

The arrangement of the different parts is indicated in fig. 1; L_1, L_2, P_1 and P_3 are rigidly fixed and stationary, while the ocular O and the prism P_2 are movable,—the ocular for focusing purposes and the prism P_2, by means of the fine micrometer screw M_1, for the purpose of measurement. It is imperative that the construction of the instrument be rigid throughout. In the trial instruments thus far used, the material has been either thick hard wood or a brass cylinder, and of these the brass cylinder is undoubtedly the more practical. The three reflecting prisms P_1, P_2 and P_3 are supported on their hypothenuse sides by brass blocks faced with cork, and these in turn are adjustable on a brass plate. By this method, the centering and adjusting of the optical parts can be accomplished at any moment accurately and with little trouble. The base line of the instrument to which all measurements are referred is the distance L_1 L_2 and its length should remain unchanged at all temperatures. Unless the instrument is made of some non-expansible material, as invar steel, however, this condition cannot be fulfilled, but for practical purposes the minute changes in length which the slight temperature variations produce may be neglected, since the instrument itself is not one of exceeding accuracy.

Assuming the distance L_1 L_2 of fig. 1 to remain constant, the theoretical accuracy of the instrument for different distances is not difficult to ascertain. In fig. 1, let $L_1 L_2 = a$, then in the triangle CDA the side $CD = \frac{a}{2}$. Since the distance of the object is always great with respect to the base of the instrument L_1 L_2 the angle, L_1-object-L_2, is small and the triangle DCA may be considered without sensible error similar to triangle L_1-Obj.-L_2. Accordingly

$$\frac{L_1\text{-Obj.}}{L_1\ L_2} = \frac{CD}{DA} \qquad (1)$$

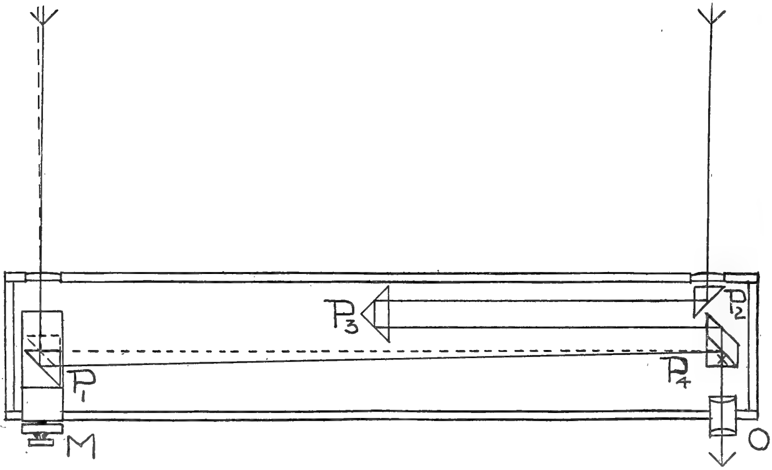
Let distance of object L_1-Obj.$=y$ and movement of micrometer screw $AD=x$, then

$$\frac{y}{a} = \frac{a}{2\,.\,x} \quad \text{or}$$

$$y = \frac{a^2}{2x} \qquad (2)$$

To find the relative accuracy of the instrument for different

Fig. 3.



distances y for a given small increment of x, equation (3) may be differentiated.

$$dy = -\frac{a^2}{2}\frac{dx}{x^2} \qquad (3)$$

Since absolute values only are considered and not the fact that x and y are counted in opposite directions, the negative sign of equation (3) may be disregarded. On substituting the value of x from (2) in this equation, we obtain

$$dy = \frac{2y^2}{a^2}\,.\,dx \qquad (4)$$

which states that the sensitiveness of the instrument decreases with the square of the distance and increases with the square of its length.

In the trial telemeter of fig. 1, the distance $L_1\ L_2=a$ is $93{\cdot}5^{\text{cm}}$ or about 1 meter. The micrometer screw reads to

·005^{mm} and actual tests with the instruments show that changes produced in the field by a movement of ·01^{mm} of the micrometer screw can be readily detected. dx is therefore ·01^{mm} or ·0001 M, and equation (4) reads

$$dy = 2 \cdot y^2 \cdot 00001$$

or

$$dy = \cdot 00002 \,.\, y^2$$

At a distance of 50 meters, therefore, the probable error of the instrument is ·05 M, or ·1 of one per cent; at 100 M, ·2 M of ·2 of one per cent; at 1000 M, 20 M, or 2 per cent.

In fig. 3, a slightly different disposition of the reflecting prism is shown which for a given base line is twice as accurate as that of fig. 1, the entire base line a being used to produce deflections of x instead of $\frac{a}{2}$ as in fig. 1. For this modification the equation reads, therefore,

$$y = \frac{a^2}{x}$$

and

$$dy = \frac{y^2}{a^2} \,.\, dx$$

The form of the prism pair P_4 in fig. 3 is slightly different from that in fig. 1, but can be ground with equal ease.

From the diagrams it is apparent that the images from L_1 and L_2 do not form in precisely the same planes and are theoretically, therefore, never in perfect focus at one and the same time, except for objects at an infinite distance. Experience has shown, however, that if the instrument be adjusted for ordinary distances, this defect is not serious, especially if a low power ocular or magnifying lens of 2 to 5^{cm} focal length be chosen.

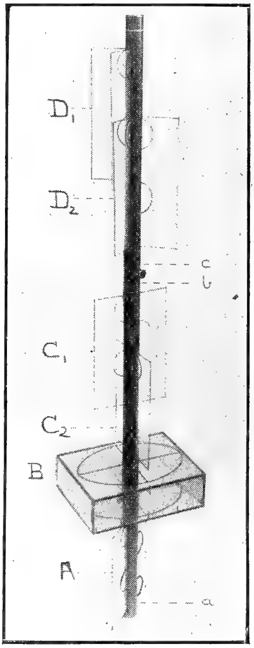
The inverted image produced by the instrument as shown in the figures can be made upright by the use of a Rochon prism pair directly in front of the ocular. The inverted image, however, is not a serious defect and equally good results can be obtained without the use of the extra prism pair, which encumbers the instrument and adds another adjustable part to be looked after.

Equation (3) shows that the accuracy of the instrument increases with the square of its length. It seems entirely feasible, therefore, to construct an instrument one or two meters in length on the principle of fig. 3, with which distances of points within a radius of one or two kilometers or miles can be read off directly with considerable accuracy, thus accomplishing stadia measurements from the transit station without the aid of a rodman.

Geophysical Laboratory, Carnegie Institution of Washington,
Washington, D. C., June, 1908.

ART. XLIX.—*A Device to Aid in the Explanation of Interference Phenomena*; by FRED. EUGENE WRIGHT.

STUDENTS of crystal optics, on taking up the subject of birefringence, frequently encounter difficulty in forming a clear conception of the exact course of the light waves through the crystals and the resultant interference phenomena when polarizer and analyzer are used (crossed nicols). The small apparatus of fig. 1 has been found serviceable as a model in this connection, and facilitates to a certain degree the explanation of several of the phenomena of plane-polarized light.



The device consists essentially of a brass rod divided into three parts, *a*, *b*, *c*, which are so connected that each one is revolvable for itself about the common axis; into each section, moreover, longitudinal slits have been cut and plates of thin, transparent celluloid inserted. The celluloid plate A represents the plane of vibration of light waves emerging from the lower nicol of the microscope; B is a celluloid model of the crystal section with its ellipsoidal axes at an angle of 45° to the plane of vibration of the lower nicol; C_1 and C_2 represent the planes of the two waves emerging at right angles to each other from the crystal plate, the light waves C_1 being a definite distance ahead of C_2 as a result of the unequal velocities of the two waves in their passage through the crystal B. On entering the upper nicol, these two waves are again reduced to the common planes of vibration D_1 and D_2, the waves vibrating along D_2, however, being destroyed by total reflection and those along D_1 only passing through. By the use of this model, it is not difficult to prove: (1) that two waves emerging from a refracting crystal at a distance apart of one or more whole wave lengths (phase difference zero) interfere mutually when reduced to the common plane of vibration, D_1; (2) while two waves one-half wave length apart (in opposite phase) mutually strengthen each other when reduced to the common plane of vibration, D_1, of the upper nicol; vice versa, if the plane D_2 be considered, the phenomena are exactly reversed—facts which are difficult to represent clearly without the aid of some such model.

Geophysical Laboratory, Carnegie Institution of Washington,
Washington, D. C.

ART. L.—*Descriptions of Tertiary Plants, II*; by T. D. A. COCKERELL.

THE plants discussed below are all from the North American Miocene. They represent a flora containing many genera at that time widely spread over the Holarctic Region, but in later times driven southward, and to-day existing in much more limited areas; some in Asia, others in various parts of America. They show very clearly that many of the ostensibly endemic genera of various regions may well have originated elsewhere, and are merely making their last stand where we now find them.

FIG. 1.

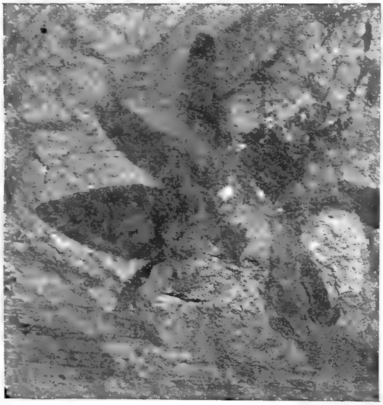


FIG. 1. *Geaster florissantensis.*

FIG. 2.

FIG. 2. *Pinus sturgisi.*

FUNGI.

Geaster florissantensis sp. nov. Fig. 1.

Diameter of "star" about 56^{mm}, the segments about eight in number, five being visible, variable in form, the largest 20^{mm} long and about $11\frac{1}{2}$ broad at base, but one next to it only about 7 broad; color dark brown, texture apparently leathery, without any sign of venation.

Florissant, at a new station on the hillside not far from 20 (*W. P. Cockerell*, 1908). It occurs on a slab with numerous remains of *Typha lesquereuxi* Ckll., *Ulmus hilliæ* Lx., and other plants. The appearance is exactly that of a modern *Geaster* in the expanded condition, and the irregularity of the segments is unlike that of any calyx known to me. *Geaster* is, of course, common in Colorado to-day.

GYMNOSPERMS.

Pinus sturgisi sp. nov. Fig. 2.

Leaves in bundles of threes, apparently entire-margined, about 175^{mm} long and $1\frac{2}{5}^{mm}$ broad, very straight, sharp-pointed. Two fibrovascular bundles are very distinct, being preserved as white lines. In all respects, the plant agrees very closely with the living *P. tæda* L., of the Eastern and Southern States.

Florissant; the type from Station 13 B (*Miss Gertrude Darling*, 1908), but the species was also found, less well preserved, at various stations in 1907. The species is dedicated to Dr. W. C. Sturgis, of the School of Forestry at Colorado College, in recognition of his contributions to Colorado botany. The fossil species of *Pinus* from Florissant must now be considered to be three in number at least, separable as follows:

Leaves in bundles of five .... *P. wheeleri* Ckll. (doubtfully recorded as *P. palæostrobus* (Ett.) Heer, by Lesquereux).
Leaves in bunches of three .... 1.
1. Leaves about 175^{mm} long .... *P. sturgisi* Ckll.
Leaves about 70^{mm} long .... *P. hambachi* Kirchner.

I formerly sunk *P. hambachi* under *P. florissanti* Lx., which was based on a cone, but it must be restored, at least provisionally.

Heyderia C. Koch.

This genus, once widespread, is restricted to the Pacific coast region of North America (*Heyderia decurrens* (Torrey) C. Koch) and China (*H. macrolepis* = *Libocedrus macrolepis* Benth. and Hook. = *Calocedrus macrolepis* Kurz). At

Florissant, Colorado, it is represented in the Miocene by *H. coloradensis* Ckll., while in the Miocene of Europe, at Radoboj, *Heyderia salicornioides* (*Libocedrus salicornioides* Heer) is very well preserved. Other species, supposed to belong here, are from the Upper Cretaceous of Greenland and the Miocene of Spitzbergen.

ANGIOSPERMS.

Ailanthus americana sp. nov. Fig. 3.

Samara about 38^{mm} long, 9 broad; seed 6^{mm} long and a little over 4 broad, placed with its long axis about 15 degrees from axis of samara; venation of wings well preserved, agreeing with that of *A. glandulosa* L.; apical part with a thickening along one side, as in Lesquereux, Cret. and Tert. Floras, Pl. xl, f. 7.

FIG. 3.

FIG. 3. *Ailanthus americana.*

FIG. 4.

FIG. 4. *Quercus knowltoniana.*

Florissant, Station 13 B, 1903. Type at University of Colorado.

Ailanthus (wrongfully called *Alianthus* in Knowlton's Cat. Cret. and Tert. Pl.) is at present confined to Asia, with three species. It is well represented in the Tertiary beds of Europe, and is credited with two American Tertiary species, one from the Miocene of Oregon, the other from the Green River beds of Wyoming. The Oregon species is very distinct from ours; that from Wyoming is based on a supposed leaflet with a remarkably long petiole, which seems to be doubtfully of this genus. However, Lesquereux figures with his *A. longepetiolata* a samara, which he says "may not represent the fruit of the same species," but which is evidently very much like that from Florissant. The seed is more transverse, however; the venation is not shown.

Quercus knowltoniana sp. nov. Fig. 4.

Acorn-cup 30^{mm} diameter; scales in about 10 rows, triangular, from about the fifth row sharp-pointed, but the more basal ones broad and angled rather than pointed; no visible marginal fringe.

Florissant (*Mrs. Charlotte Hill*). Holotype at Yale University, Cat. No. 1005. I had retained this curious fossil for months, hoping to be able to determine it, but failing to recognize its relationships. Dr. F. H. Knowlton recently visited my laboratory, and upon showing the fossil to him, he at once recognized what it was. Now that the fact has been pointed out it is so evident that the specimen is an acorn-cup that I do not understand my obtuseness on the subject. The species recalls the recent *Q. macrocarpa* Michx., the cups of which grow to an even larger size. I have no leaf from the shale that I can refer to it. The cup was evidently widely open and shallow, not partially closed as it is in *Q. lyrata.* Fossil acorn-cups have been found in the Miocene of Europe (*Q. palæocerris* Sap., *Q. subcrenata* Sap.).

Rosa ruskiniana sp. nov. Fig. 5.

Represented by a bud about 16^{mm} long, and six in diameter. Hypanthium subglobose, no doubt producing a practically spherical fruit, covered with minute spines; sepals with very large and thick-stalked glands or gland hairs on the basal half, these very much larger than the spines of the hypanthium; apical portion of sepals long, with three or four large lobes on each side.

Florissant, Station 13 B (*W. P. Cockerell*, 1908). By the character of the hypanthium this is evidently related to *Rosa cherokeensis* Donn., but the sepals are strongly lobed. Such a rose would have trifoliate leaves, and these should resemble those of *R. hilliæ* Lx., at least to a considerable degree. As, however, it is impossible definitely to connect the bud with the leaves of *R. hilliæ* (we have not found the latter), I give the former a distinctive name; dedicating it to John Ruskin, whose copy of Lindley's "Rosarum Monographia," with many marginal notes, is in my library.

Hydrangea florissantia Ckll.

Rhus rotundifolia Kirchner, Trans. St. Louis Acad., viii, p. 184, is the same thing. The name *rotundifolia* was much earlier used in *Hydrangea* by Rafinesque. Kirchner's type is, I believe, in the U. S. National Museum.

Sambucus newtoni sp. nov. Fig. 6.

Leaflet (doubtless a lateral one) about 132^{mm} long and 26 broad; texture thin, this and the venation exactly as in living species of *Sambucus;* form parallel-sided, rapidly narrowing apically to a sharp point, very much as in *S. arborescens* Nuttall; margin with exceedingly minute denticulations, 4 to 5 in 5^{mm}, and even these evanescent on the basal half.

FIG. 5.

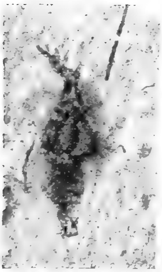


FIG. 5. *Rosa ruskiniana.*

FIG. 6.

FIG. 6. *Sambucus newtoni.*

Florissant, Station 13 B (*George Newton Rohwer*, 1908). The best side shows all but the base; the reverse lacks the apex, but shows nearly all of the base, which is substantially as in *S. arborescens.* This is the first American fossil *Sambucus;* in Europe the genus is represented by flowers in amber.

Lomatia acutiloba Lx. is on the same slab as *Sambucus newtoni.*

Anona spoliata sp. nov. Fig. 7.

Leaf apparently thick, oblong, entire, the blade 40^{mm} broad, and probably over 80 long (apex missing), the base broadly rounded, the midrib and petiole stout, the latter short, only about 9^{mm} long. Venation pinnate, the secondaries arising from the midrib at an angle mostly little less than a right angle, but varying in this respect, and gently curving upwards, terminating in submarginal arches connecting their tips, and variously enclosing areas of different shapes. Between the principal lateral veins are small and hardly noticeable ones, not proceeding far from the midrib. In the shape of the leaf, the short petiole, and the venation, this is almost exactly like the living *Anona glabra* L., of Florida. In one place two of the principal secondaries unite, as they sometimes do in *A. glabra*.

FIG. 7.

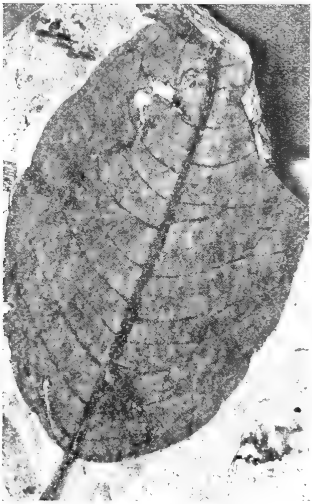


FIG. 7. *Anona spoliata.*

Florissant, Station 13 B (*Geo. N. Rohwer*, 1908). *Sabina linguæfolia* (Lx.) Ckll. occurs on the same slab. *Anona robusta* Lx., from the Laramie (?) at Golden, Colorado, is a similar species, differing, however, in the character of the submarginal venation, which does not show the large enclosed areas. The resemblance of *A. spoliata* to *A. robusta* is, therefore, not nearly so close as to *A. glabra*. The European *A.*

elliptica Unger, from the Miocene of Radoboj, is close to *A. spoliata* in respect to the submarginal venation, but very different in the cuneate base, the leaf being very like that of *Crescentia latifolia.*

Juglans leonis n.n.

Juglans californica Lx., Mem. Mus. Comp. Zool. vi, 34, pl. ix, x (1878). Miocene of California. (Not *J. californica* S. Watson, Proc. Am. Acad., x, 349 (1875).)

Rhus mensæ n.n.

Rhus metopioides Lx., Mem. Mus. Comp. Zool. vi, 31 (1878). Miocene of California. (Not *R. metopioides* Turcz., Bull. Soc. Nat. Mosc., xxxi, 1, 468 (1858).)

Salix merriami n.n.

Salix elliptica Lx., Mem. Mus. Comp. Zool. vi, 10 (1878). Miocene of California. (Not *S. elliptica* Sleich., Ser., Ess. Saul., 44; cf. Steud., nom. (1841).)

Zizyphus microphyllus Lx., and *Magnolia lanceolata* Lx., of the California Miocene, also bear preoccupied names.

Weinmannia dubiosa Ckll.

We found this at Stations 13 B and 14, at Florissant. The leaflets vary from five to seven.

Robinia brittoni sp. nov. Fig. 8.

Represented by a leaf, scarcely at all different from the living *R. pseudacacia* L. Five leaflets are preserved. Leaflets about 22^{mm} long and $9\frac{1}{2}$ broad, very briefly mucronate at apex, and with short petiolules about 2^{mm} long, which are as usual opposite, the pairs about 14^{mm} apart. From the first pair of leaflets to the insertion of the leaf is only 12^{mm}. The shortness of the petioles agrees best with *R. viscosa* Vent., but the shape of the leaflets accords better with *R. pseudocacia.* Florissant, Station 13 B (*Melford Smith*, 1908). Dedicated to Dr. N. L. Britton, who has contributed so much to our knowledge of American trees.

Robinia is to-day confined to America, but it is found fossil at Œningen and other European localities.

Menyanthes coloradensis sp. nov. Fig. 9.

Represented by a crown bearing five leaves, in form and appearance exceedingly like the living *M. trifoliata* L., but *two of the leaves are entire.* One of the basal leaf-sheaths, curled backwards, is well preserved, and exactly as in *M. trifoliata.* The whole plant is much smaller than *M. trifoliata ;* the petioles of the better-developed leaves only about 28^{mm} long, with leaflets about 30^{mm} long, and 9 to 10 broad. The prominent lateral or secondary veins are irregular, less numerous than in *M. trifoliata,* and more or less strongly arched, with the concave side upwards. The entire leaves are broad-lanceolate to ovate, the largest being over 15^{mm} broad.

Fig. 8.

Fig. 8. *Robinia brittoni.*

Fig. 9.

Fig. 9. *Menyanthes coloradensis.*

Florissant, Station 13 B (*Geo. N. Rohwer,* 1098) : also one found at the same place by Miss Gertrude Darling. *Menyanthes* is to-day a monotypical genus of Holarctic distribution. In the fossil state it is known, principally from capsules and seeds, from Greenland, Spitzbergen, and Central Europe. The occurrence of entire leaves on the fossil is of interest in view of the fact that the allies of *Menyanthes* are entire-leafed. I asked Dr. L. N. Britton whether he had ever seen entire leaves on the living species : he replied that no such had ever come under his observation. The seedling of *Menyanthes* seems not to have been described.

ART. LI.—*On Three Contact Minerals from Velardeña, Durango, Mexico. (Gehlenite, Spurrite and Hillebrandite);* by FRED EUGENE WRIGHT.

DURING the summer of 1907, a geologic examination of the Velardeña mining district in Mexico was made by Mr. J. E. Spurr, assisted by Mr. G. H. Garrey. Several of the thin sections of the material there gathered were sent to the writer for examination, and in one of these a mineral with peculiar optic properties was observed. At the suggestion of the writer an adequate collection of the rock from which the thin section had been cut, was then made by Mr. Garrey, and in this collection the three minerals to be described below were found. Two of these minerals proved to be new mineral species, silicates of interesting composition, while the third, gehlenite, is apparently novel for this continent. All three are contact minerals, formed near the junction of altered limestone and intrusive basic diorite and their relations to the contact and conditions of formation have been carefully studied by Messrs. Spurr and Garrey. As the results of their extended investigation will soon be ready for publication it has not been deemed necessary to consider in detail in this present paper conditions of occurrence and formation of these minerals and their relations to the ore deposits in general.

The chemical analyses of the three minerals and their specific gravity determinations were made by Dr. E. T. Allen of the Geophysical Laboratory, and to him the writer is deeply indebted for the courtesy.

Gehlenite.[*]

This mineral occurs in massive granular aggregates, usually dark gray or gray-black in color, from minute inclusions of magnetite and other particles. Rarely small pieces of gehlenite of amber-yellow color and free from magnetite inclusions were observed. The grains are rounded in outline and not suitable for crystallographic measurement. The physical and optical properties, however, are similar to those recorded for gehlenite from other localities, and the chemical composition also agrees as well with the prescribed formula as the analyses of the type material.

Crystal system, probably tetragonal, judging from the cleavage, which is imperfect after 001 and much less well marked after a prism. Fracture, uneven and irregular, conchoidal to splintery. Hardness, between 5 and 6, about 5·5. Luster,

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[*] Type specimen from contact aureole of the Terneras intrusion, Velardeña, Durango, Mexico.

resinous to greasy. Translucent to transparent in thin flakes; in large masses, sub-transparent to opaque. Streak white to pale gray, the gray probably due to fine magnetite inclusions.

In the thin section, the gehlenite appears weakly birefracting with comparatively high refractive index. Magnetite inclusions are abundant and often show crystal outline. The magnetite also occurs, filling cleavage and fracture cracks in the gehlenite and evidently was precipitated both before, during and after the crystallization of the gehlenite. In certain of the sections the magnetite crystals showed a distinct tendency to an arrangement parallel with the first and second order prism faces. Round earthy spots also occur filled with earthy matter and are apparently of secondary origin, although they may possibly be weathered original spherulites of some mineral earlier than the gehlenite.

In the thin section the basal cleavage is well marked and after it the crystals are often developed in thick tabular form. In thick slides the interference color becomes intensely yellow, reminding one somewhat of the peculiar yellow interference tints of certain epidotes.

In convergent polarized light the interference cross is wide and uniaxial. Optically negative. On one section the birefringence was measured at $\omega - \epsilon = 0{\cdot}0055$. The refractive indices were measured directly on an Abbé Pulfrich total refractometer in Na light and found to be $\omega = 1{\cdot}666 \pm {\cdot}003$ and $\epsilon = 1{\cdot}661 \pm {\cdot}003$. These values were obtained by using a polished plate of the granular material, and the refractive indices could not be determined under such conditions with an accuracy greater than ± ·003.

The specific gravity at 25° was determined on two samples by pycnometric methods at 3·029 and 3·049 with an average = 3·039. Part of this variability is probably the result of differences in relative amounts of inclusions.

On uncovering a thin section and treating the exposed surface with weak hydrochloric acid and then, after thorough rinsing, with a solution of fuchsin, the gehlenite was found to have gelatinized slightly. This fact was corroborated by a chemical test with powdered material, which was found to gelatinize readily.

The following chemical analysis does not agree with any simple formula and a comparison of other gehlenite analyses indicates that under the term gehlenite a solid solution series between several different end members is probably included.

Compared with the other analyses, the Velardeña gehlenite is somewhat lower in silica and magnesia, and higher in alumina and lime, but otherwise very similar, and is essentially a calcium aluminum silicate.

Chemical Analysis.

	1	1a	2	3	4
SiO_2	26·33	·4359	29·78	28·59	31·40
TiO_2	·03	·0004			
Al_2O_3	27·82	·2722	22·02	22·32	22·32
Fe_2O_3	1·43	·0089	3·22		
FeO	·50	·0070	1·82	0·37	0·03
MnO	·01	·0001	----	0·50	0·96
MgO	2·44	·0605	3·88	7·78	10·02
CaO	39·55	·7050	37·90	36·76	30·92
Na_2O	·21	·0035	----	0·40	1·17
K_2O	·10	·0009	----	0·21	0·12
H_2O	1·85	·0103	1·28	----	
CaS	----	----	----	3·25	3·85
CO_2	none	----	----	----	----
	100·27	1·5047	99·90	100·18	100·79

1. Gehlenite, Velardeña, Mexico. E. T. Allen analyst.
1a. Molecular proportions of 1.
2. Gehlenite, Monzoni, Rammelsberg, Mineralchem., 1875, 604.
3. Gehlenite, Falkirk, Sweden. Edg. Jackson in Bauermann, Journ. Iron and Steel Inst., 1886, i, 88.
4. Gehlenite, Clarence, J. H. L. Vogt, Stud. Slagger, Stockholm, 1884, 138.

Before the blowpipe thin slivers of this mineral melt down with difficulty to dark, non-transparent beads, give a pronounced calcium flame reaction and glow intensely.

In the hand specimens, gehlenite occurs either practically alone except for magnetite inclusions, or together with spurrite, yellow garnet and calcite. Later veinlets consisting chiefly of calcite were noted occasionally, cross cutting the specimens.

So far as the writer has been able to ascertain from the available literature, this occurrence is the first recorded for gehlenite on this continent.

*Spurrite.**

This mineral, like gehlenite, occurs in granular masses which at first glance might be mistaken for crystallized marble, especially since the cleavage faces frequently glisten in the sunlight like those of calcite. No crystals were observed and the only goniometric measurements possible were made on cleavage fragments. Two cleavages were observed, the one good and the second much less perfect. The reflection signals from these faces were not of equal value and the cleavage

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* Type specimen from contact aureole of Terneras intrusion, Velardeña, Durango, Mexico.

angle could only be obtained approximately; the best average of the results is 79° with a probable error of at least $\pm \frac{1}{2}^\circ$. Fracture uneven to splintery. Brittle. Hardness, about 5. Luster, vitreous to resinous. Color, pale gray with tints of blue or yellow to colorless. Transparent to translucent. Streak, white.

On the hand specimens a weathering or alteration crust, consisting chiefly of finely divided carbonate, occurs not infrequently. In the thin section the spurrite is well defined optically and is excellent material for optical work.

From the relations of the optic properties to the crystallographic it is highly probable that spurrite is monoclinic and that the cleavage faces are parallel with the orthodiagonal (*b* axis). If the good cleavage plane be called the basal pinacoid, the optical orientation is apparently the following: $b = \mathfrak{a}$; $a : \mathfrak{c}$, very small and possibly zero, the cleavage cracks not being sufficiently perfect for decisive measurements.

FIG. 1*a*.

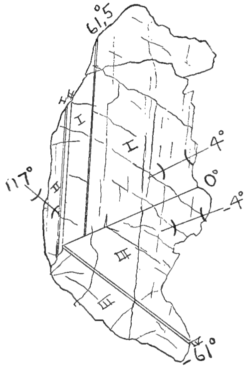
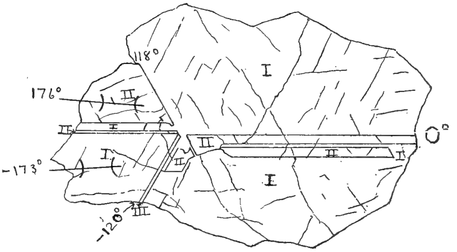


FIG. 1*b*.



Twinning after both 001 and polysynthetic twinning after orthodomes at angles of 56° to 58° with the twinning lines of 001 occur, and occasionally divide the field into sextants of the same birefringence and all cut approximately normal to the acute bisectrix, the plane of the optic axes in the different sextants occupying different positions, as shown in the accompanying sketches. (Figs. 1*a*, 1*b*.)

The polysynthetic lamellae are often extremely fine and resemble albite lamellae very closely. On a section almost precisely normal to the acute bisectrix the angle between the plane of the optic axes and the fine twinning lamellae was measured at 57°·5 in sodium light. On this thick plate crossed dispersion was unusually clearly marked, the angle between the plane of the optic axes for red lithium light being about 57°·6, and for green thalium light 57°·1. These measurements indicate a dispersion of the bisectrices $\mathfrak{c}_\rho : \mathfrak{c}_{gr}$ in the plane of symmetry of about 0·15°. At the same time a slight dispersion of the optic axes was noticeable with $2E_\rho > 2E_v$.

The optic axial angle was measured on a number of different sections by the use of the double screw micrometer ocular and also of the universal stage, the average being $2V = 39°·5, \pm 1°$; whence $2E = 70°$. Owing to the strong birefringence the interference figure is unusually well marked even in normal thin sections. The refractive indices were measured in sodium light on several different plates on an Abbé-Pulfrich total refractometer with reducing attachment, the different refractive index lines from the polished plates being clearly marked and easy to follow:

$$\begin{array}{llll} \gamma\ \mathrm{Na} = 1{\cdot}679 \pm {\cdot}002 & & \gamma - \alpha = {\cdot}039 \\ \beta\ \mathrm{Na} = 1{\cdot}674 \pm {\cdot}002 & & \gamma - \beta = {\cdot}005 \\ \alpha\ \mathrm{Na} = 1{\cdot}640 \pm {\cdot}002 & & \beta - \alpha = {\cdot}034 \end{array}$$

From these values the calculated optical axial angle is $2V = 41°\ 12'$, which agrees fairly well with the measured value. Optical character negative.

The birefringence values were checked by direct measurements on plates in the thin section and closely accordant results obtained.*

$$\begin{array}{l} \gamma - \alpha = {\cdot}040 \\ \beta - \alpha = {\cdot}036 \end{array}$$

In the thin section spurrite is recognized by its high birefringence, imperfect cleavage and small optic axial angle with negative optical character and in thick sections noticeable crossed dispersion.

Still further evidence on the crystal system of spurrite was gathered from etch figures on the good cleavage face. Cleavage flakes were immersed for 10 seconds in cold 5 per cent hydrochloric acid and the etch figures of fig. 2 obtained.

Many of these figures appear asymmetrical but the upper terminal endings are so variable and influenced by adjacent cleavage cracks to such an extent that the general symmetrical aspect of the figure with respect to a vertical plane of symmetry may have thus been disturbed. It must be admitted, however, that the etch figures may be actually asymmetric, in

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* For these direct measurements of birefringence in the thin section the writer is indebted to Mr. E. S. Larsen, Jr., of the Geophysical Laboratory.

which case spurrite is triclinic instead of monoclinic; the relations of the optic properties for different wave-lengths are then

Fig. 2.

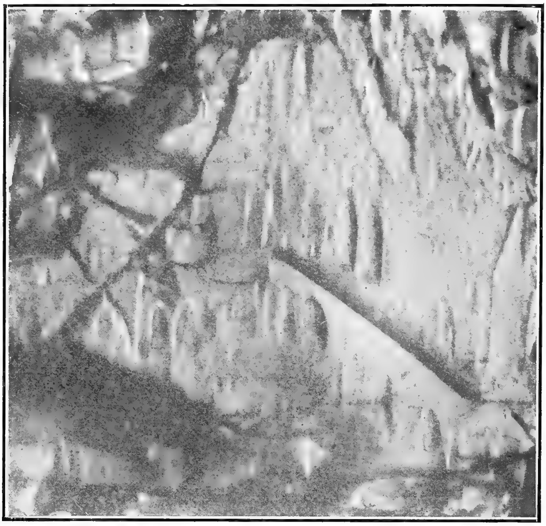

Fig. 2.—Etch figures on good cleavage face of spurrite produced by 10 sec. immersion in cold 5 per cent HC1. Magnification 150 diameters.

	1	1*a*	2
SiO_2	26·96	·4467	27·13
TiO_2	·01	·0001	
Al_2O_3	·39	·0038	
Fe_2O_3 FeO	·11	·0007*	
MnO	·03	·0004	
MgO	·23	·0058	
CaO	62·34	1·1114	62·98
Na_2O	·05	·0008	
K_2O	trace	-----	
H_2O	none	-----	
CO_2	9·73	·2212	9·89
	99·85	1·7909	100·00

*Calculated as Fe_2O_3.

1. Spurrite, Velardeña, Durango, Mexico, E. T. Allen analyst.
1*a*. Molecular proportions of 1.
2. Theoretical percentage weight composition for the formula $2Ca_2SiO_4.CaCO_3$.

such as to simulate very closely crossed dispersion of the monoclinic system.

Before the blowpipe spurrite shows strong calcium flame reaction, loses its glassy lustre, becomes white and porcelain-like but does not fuse even in thin splinters.

Spurrite effervesces readily with weak hydrochloric acid, dissolves completely and gelatinizes thoroughly. The chemical analysis was made on carefully selected material.

The agreement of the analyzed material with the formula $2Ca_2SiO_4.CaCO_3$ is remarkably close and in view of the purity of the material analyzed can leave no doubt that spurrite is a compound of the above formula.

The specific gravity at 25° was determined with pycnometer, both in xylene and in water, and the following results obtained:

$$\begin{array}{rl} \text{Spec. gr. at } 25^\circ \text{ in xylene} = & 3{\cdot}013 \\ \text{`` `` `` `` water} = & \left\{\begin{array}{l} 3{\cdot}014 \\ 3{\cdot}016 \end{array}\right. \\ \hline \text{Average spec. gr. at } 25^\circ = & 3{\cdot}014 \end{array}$$

Spurrite occurs in the hand specimens either in pure, unaltered state, except for minute inclusions of magnetite, or together with yellow garnet, calcite and gehlenite. Its weathering products consist chiefly of carbonates in microscopic aggregates, which appear first along cracks and cleavage planes in the altering mineral.

Through the courtesy of Mr. E. S. Shepherd of the Geophysical Laboratory, several experiments were made to reproduce spurrite artificially by heating ten per cent solutions of sodium chloride with pure Ca_2SiO_4 and $CaCO_3$ in finely divided state and in different proportions in silver-lined steel bombs from 6 to 9 days at temperatures of 350° to 400°. Although minute, well-shaped crystals were obtained in many of the preparations with refractive indices α and γ, practically identical with those of spurrite, the symmetry was orthorhombic and therefore not that of spurrite. Synthetic experiments on this compound are still in progress.

This mineral is named in honor of Mr. J. E. Spurr of New York, who collected the original material and who has done much to further existing knowledge of ore deposits and their accompanying minerals.

*Hillebrandite.**

Hillebrandite, unlike spurrite and gehlenite, is distinctly a fibrous mineral and occurs in aggregates often as radial spheru-

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* Type specimens from the 8th level of the Terneras Mine, Velardeña, Durango, Mexico.

lites, the individual fibers of which are difficult to separate satisfactorily, and rarely measures $\cdot 5^{\mathrm{mm}}$ in length. In the hand specimen, especially when examined with a lens, these fibers tend to produce a faint silky luster on the otherwise vitreous to porcelain-like mass. Cleavage, so far as could be observed, prismatic. Brittle. Hardness between 5 and 6, about 5·5. Color, pure porcelain white, often with faint tinge of pale green. Translucent in small chips. Streak, white.

Under the microscope the optic properties are those of aggregates of fibers, often in approximately parallel orientation, rather than of a single fiber. As a result the optical data are not easy to determine with great accuracy, although certain features of the mineral are so characteristic that its determination as such is a relatively simple matter.

The refractive indices γ and α were measured in sodium light on an Abbé-Pulfrich total refractometer on a polished plate of the mineral. It has been found by experience that even in the case of such fine-grained masses as hillebrandite, the phenomena in sodium light on the refractometer are sufficiently distinct, when reducing attachment is used, to permit a fairly accurate determination of the two limiting curves γ and α, although in the flood of light from the different grains, the medium refractive index line does not appear with sufficient distinctness to allow of its determination. On such a plate the refractive indices were found to be

$$\gamma = 1{\cdot}612 \pm {\cdot}003$$
$$\alpha = 1{\cdot}605 \pm {\cdot}005$$

The birefringence is medium to weak, but difficult to determine directly because of interweaving of overlapping fibers.

The extinction is parallel, the ellipsoidal axis ($\mathfrak{c}$) being invariably parallel with the fiber direction which at the same time is the cleavage direction. The optic axial angle is not very large, $2E_\rho$ being possibly between 60° to 80°, while the dispersion of the optic axes is unusually strong and gives rise to peculiar, abnormal blue interference colors resembling those in certain epidotes and characteristic of hillebrandite. The optic character is negative with $2E_v > 2E_\rho$. The plane of the optic axes was found to vary, being in the one plate parallel with the fiber direction and in the next perpendicular to the same, an abnormal phenomenon which may be due in whole or in part to the disturbing influence of the interlacing fibers which tend to veil the optic phenomena and often most effectively. On a section normal to the acute bisectrix the plane of the optic axes was parallel with the cleavage and direction of elongation.

From these optical and crystallographic data, it appears that hillebrandite is orthorhombic with possibly $c=\mathfrak{c}$, $a=\mathfrak{a}$ and cleavage after 110 (?). Its most characteristic optic features are: refractive index about 1·61, birefringence weak to medium, 2E medium with very strong axial dispersion $2E_v > 2E$, which in parallel light gives rise to abnormal blue interference tints which are readily recognized. Optical character, negative.

The absence of crystallographic faces of any degree of perfection precluded any attempts at etching which might have been made.

The specific gravity at 25° was determined by pycnometer with water at 2·692, and also in xylene at 2·692. The check determination in xylene was made because the analysis of hillebrandite shows it to have been slightly hydrolized.

In hydrochloric acid (1:1) hillebrandite separates some silica at once but enters otherwise into solution. Hillebrandite decomposes very slowly with cold water as the test by adding a few drops of phenolphthaline to the mixture indicates.

Before the blowpipe thin splinters of hillebrandite fuse down with difficulty to a colorless glassy bead, at the same time giving a strong calcium flame reaction and glowing briskly.

CHEMICAL ANALYSIS.

	1	1*a*	2
SiO_2	32·59	·5398	31·74
TiO_2	·02	·0003	
Al_2O_3	·23	·0023	
Fe_2O_3 FeO	·15	·0009*	
MnO	·01	·0001	
MgO	·04	·0010	
CaO	57·76	1·0296	58·81
Na_2O	·03	·0005	
K_2O	·05	·0005	
H_2O	9·36	·5019	9·45
F	none		
CO_2	none		
	100·24	2·0769	100·00

1. Hillebrandite, Terneras Mine, Velardeña, Durango, Mexico, E. T. Allen analyst.

1*a*. Molecular proportions of 1.

2. Percentage weight composition of formula $H_2O.2\ CaO.SiO_2$.

* Calculated as Fe_2O_3.

This analysis agrees closely with the formula $Ca_2SiO_4.H_2O$,* it being a little higher in silica and lower in lime, a condition which is evidently due to a slight leaching of the lime. The water of the analysis was determined by loss in weight, the figure given being the average of two determinations, 9·34 and 9·39. By absorption by calcium chloride plus the little obtained at 110° the result was 9·18. The first figures, however, are more accurate.

Hillebrandite occurs usually with few inclusions and even magnetite is rare. Occasionally small grains of carbonate, yellow garnet and wollastonite occur with it and also earthy material of a secondary nature. Veinlets of wollastonite traversed several of the hand specimens and in each case the direction of elongation of the wollastonite fibers was normal to the vein walls.

Experiments to produce hillebrandite synthetically have thus far not proved successful.

The above optical and chemical data show beyond question that hillebrandite is a true chemical compound of unique chemical composition. It is with great pleasure, therefore, that the writer suggests the above name as a token of appreciation of the fundamental researches of Dr. W. F. Hillebrand of the U. S. Geological Survey in mineralogical chemistry.

Geophysical Laboratory.
Carnegie Institution of Washington,
Washington, D. C.
June, 1908.

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* This formula may also be written $CaSiO_3.Ca(OH)_2$ or simply $H_2O.2CaO.SiO_2$.

ART. LII.—*The Volumetric Estimation of Potassium in Animal Fluids;* by W. A. DRUSHEL.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cxcii.]

THE distribution of potassium in plant and animal tissues has been studied by Macallum* and others. Macallum precipitated potassium in place as potassium sodium cobalti-nitrite, an insoluble potassium salt which by its crystalline form and color is easily recognizable under the microscope. To study the function of potassium in the animal organism it is desirable to have a simple and rapid method for its estimation in the various tissues and fluids. A number of quantitative methods have been proposed which, however, are not wholly free from objections.

M. Kretschy, in 1876, after having carefully studied the several indirect methods for potassium and sodium in the presence of each other, finally adopted a modification of the chlorplatinate method for potassium in the presence of relatively large amounts of sodium in physiological work. He worked with quantities of potassium ranging from 3 mgrm. to 120 mgrm., precipitating it as the chlorplatinate in the usual manner. The washed and dried precipitate was carefully ignited, the residue extracted with water and the extract evaporated to dryness. This residue was gently ignited and weighed as potassium chloride. A small amount of platinum usually passed through the filter, giving a result which was too high for potassium chloride. To avoid error on this account the weighed potassium chloride was dissolved in water, any residue of platinum filtered off on ashless paper, ignited and weighed, and the necessary correction made in the weight of the potassium chloride.

Some years later Lehmann,† Bunge,‡ Heintz,§ and Pribram and Gregor‖ used different modifications of the Fresenius chlorplatinate method for the estimation of potassium in urine. In the methods of Lehmann, Bunge, and Pribram and Gregor the sulphate radical was removed by an excess of barium hydroxide or barium chloride; subsequently the excess of barium was removed by ammonium carbonate and ammonium hydroxide, or in case of barium hydroxide by carbon dioxide. Lehmann evaporated the urine with ammonium sulphate before ashing the residue, while Bunge treated the urine directly with barium hydroxide. Pribram and Gregor oxidized the organic matter by heating the urine, acidified with sulphuric acid, to

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* Jour. of Physiol., xxxii, 95 (London).

† Zeitschr. physiol. Chem., viii, 508.

‡ Zeitschr. Biologie, ix, 139.

§ Pogg. Ann., lxvi, 133.

‖ Zeitschr. anal. Chem., xxxviii, 409.

the boiling point and adding an excess of potassium free barium permanganate. Heintz treated 20^{cm^3} to 30^{cm^3} of clear urine with chlorplatinic acid and a threefold volume of a 1 : 4 ether and absolute alcohol mixture. After standing 24 hours the precipitate was filtered off, washed with alcohol, dried, ignited and weighed. The residue was then extracted with hot water and again dried and weighed. The amount of potassium chloride was found by taking the difference of the weights. It has been repeatedly shown that appreciable amounts of the alkali salts are carried down by barium sulphate, which can not be completely removed by washing. This objection applies to all of the methods in which the sulphate radical is removed by means of a barium salt. The loss of alkalis is especially appreciable where a large amount of barium sulphate is formed in the presence of relatively small amounts of the alkali salts.

In 1898 K. Gilbert devised a method for the separation of potassium which does not require the previous removal of the sulphate radical. He treated a potassium salt solution free from mineral acids with an excess of sodium cobalti-nitrite acidified with acetic acid. After standing from 12 to 20 hours the potassium was quantitatively separated out as potassium sodium cobalti-nitrite which could be freely washed with cold water without an appreciable loss. Gilbert decomposed this precipitate by heating with dilute hydrochloric acid and estimated the potassium as the perchlorate or chlorplatinate.

A few years later Autenrieth and Bernheim[*] used Gilbert's method for separating potassium in urine, subsequently estimating the potassium as the perchlorate. They used 6^{cm^3} to 10^{cm^3} of concentrated sodium cobalti-nitrite to precipitate the potassium in 50^{cm^3} of urine. At this dilution it had been shown by Gilbert that the potassium is quantitatively precipitated and that the precipitate is apparently of indefinite composition. In 1900, however, Adie and Wood[*] found that with a sufficiently high concentration of the reagent and of the potassium salt solution a precipitate of definite composition, represented by the formula $K_2NaCo(NO_2)_6.H_2O$, is obtained. They further found that by decomposing this precipitate with boiling dilute sodium hydroxide and titrating the nitrites with standard potassium permanganate the potassium may be estimated with a fair degree of accuracy.

In a previous paper[*] from this laboratory it was shown that it is unnecessary, after adding the cobalti-nitrite reagent, to let the mixture stand from 12 to 20 hours, if it is evaporated nearly to dryness, also that the precipitate may be directly oxidized with potassium permanganate without previously decom-

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[*] Zeitschr. physiol. Chem., xxxvii, 39. [†] Jour. Chem. Soc., lxxvii, 1076.

[‡] This Journal, xxiv, 433, 1907.

posing it with boiling sodium hydroxide. Later it was found that a half saturated sodium chloride solution is preferable to cold water for washing the precipitate since it permits the use of a coarser asbestos felt in filtering without danger of loss.

The method used in the work on animal fluids is as follows: A potassium salt solution was obtained free from mineral acids and ammonia salts and treated with a liberal excess of concentrated sodium cobalti-nitrite in an evaporating dish. The mixture was evaporated to a pasty condition over the steam bath. After cooling the residue it was stirred up with enough cold water to dissolve the excess of sodium cobalti-nitrite. The precipitate was permitted to settle a few minutes, then it was filtered on asbestos in a perforated crucible and washed with the sodium chloride solution until the filtrate came through colorless. The precipitate and felt were transferred by means of a spray of water and a stirring rod to a beaker containing a measured amount (being an excess) of standard decinormal or fifth normal potassium permanganate, diluted about ten times and heated nearly to boiling. The permanganate solution was kept hot and stirred to facilitate the solution and oxidation of the precipitate, the oxidation being completed by adding 5^{cm^3} to 10^{cm^3} of dilute sulphuric acid and stirring for a minute or two. The excess of permanganate was then bleached by a measured amount of standard decinormal oxalic acid, and the solution titrated to color with standard permanganate. In this process the cobalt is reduced to the bivalent condition and the nitrites oxidized to nitrates, from which by a simple calculation it is found that one cubic centimeter of strictly decinormal permanganate is equivalent to 0·000857 grm. of K_2O.

The modified Lindo-Gladding method was used as a control in the experimental work of this paper. The potassium was obtained as the sulphate in the presence of sodium sulphate, and possibly traces of calcium and magnesium sulphate. The solution of these sulphates was treated with an excess of chlorplatinic acid, evaporated nearly to dryness, and the precipitate washed free from the excess of chlorplatinic acid with 85 per cent alcohol. The precipitate was then washed three or four times with a 20 per cent solution of ammonium chloride saturated with potassium chlorplatinate, and finally again two or three times with 85 per cent alcohol. By this treatment the sodium sulphate and the small amounts of calcium sulphate and magnesium sulphate are completely removed.

A. *Potassium in urine.*

The following table gives approximately the amount of the constituents present in a day's excretion of urine of an adult in normal health and on an ordinary mixed diet:

K_2O*	2 to 4 grm.	Urea	30 grm.
NaCl	10 “ 15 “	Uric acid	0·7 “
CaO and MgO	0·8 “	Creatinine	1·5 “
NH_3	0·7 “	Hippuric acid	0·7 “
P_2O_5 (phosphates)	1·5 “	Other organic bodies	2·1 “
H_2SO_4 (sulphates)	2·5 “		

In this list of constituents ammonia and the organic bodies, especially urea, are the only ones which should interfere with the volumetric method as previously described. To remove these bodies without the loss of potassium is apparently the only new problem.

In the experiments recorded in Table 1 aliquot portions of urine of 10 to 50 cubic centimeters each were measured with pipettes or a burette into small platinum evaporating dishes, and evaporated to dryness over the steam bath in a good draught hood. The residues of the aliquots of the first specimen were treated with 5^{cm^3} of concentrated nitric acid and again evaporated to dryness. These residues were then moistened with concentrated sulphuric acid and ignited to a white ash beginning with a low flame and increasing the heat until the organic matter was burned off, and the ammonium sulphate and excess of sulphuric acid completely removed. In subsequent experiments it was found more expeditious to treat the dried urine residue with 5^{cm^3} to 10^{cm^3} of a 9 : 1 nitric-sulphuric acid mixture, in a covered evaporating dish, removing the cover when the first violent oxidation is over, evaporating to dryness and igniting without the further addition of sulphuric acid. By this treatment the ignition of the residue from 50^{cm^3} of urine could be readily made in 30 minutes without loss of material. The residue thus prepared was treated with a little water and a few drops of acetic acid to dissolve the alkalis. Without filtering about 10^{cm^3} of concentrated sodium cobalti-nitrite were added and the mixture evaporated to a pasty condition. From this point the process was carried out as previously described. In the control experiments the phosphoric acid was removed by a slight excess of calcium hydroxide, and the calcium by ammonium oxalate, before the ignition of the residue.

The results obtained by the two methods from a number of different specimens of human urine are given in the following table.

B. *Potassium in circulatory fluids.*

An additional difficulty presents itself here in the presence of a large amount of protein material which can not be removed by coagulation and filtration without a considerable loss of

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* Taken from Hammerstein's Physiological Chemistry, (Mandel's Translation), 5th ed., p. 628.

TABLE I.

A

	Urine taken cm^3	Sp. gr.	K found grm.	K found per cent.	Method
I (1)	10	1·018	0·0124	0·12	Vol.
(2)	10	----	0·0122	0·12	“
(3)	10	----	0·0123	0·12	Grav.
(4)	10	----	0·0131	0·13	“
II (1)	10	1·022	0·0180	0·18	Vol.
(2)	10	----	0·0178	0·17	“
(3)	10	----	0·0178	0·17	Grav.
(4)	10	----	0·0171	0·17	“
III (1)	10	1·023	0·0241	0·24	Vol.
(2)	10	----	0·0242	0·24	“
(3)	10	----	0·0233	0·23	Grav
(4)	10	----	0·0231	0·23	“
IV (1)	10	1·024	0·0241	0·24	Vol.
(2)	10	----	0·0243	0·24	“
(3)	10	----	0·0242	0·24	Grav.
(4)	10	----	0·0243	0·24	“

B

	Urine taken cm^3	Sp. gr.	Vol. in 24 hrs. cm^3	K found grm.	K in 24 hrs. grm.	Method
V (1)	10	1·025	950	0·0293	2·78	Vol.
(2)	10	----	----	0·0292	2·77	“
(3)	10	----	----	0·0293	2·78	Grav.
(4)	10	----	----	0·0292	2·77	“
VI (1)	25	1·025	950	0·0740	2·81	Vol.
(2)	25	----	----	0·0747	2·84	Grav.
(3)	25	----	----	0·0740	2·81	Vol.
VII (1)	20	1·025	910	0·0757	3·44	Vol.
(2)	20	----	----	0·0752	3·42	Grav.
(3)	20	----	----	0·0764	3·47	Vol.
VIII (1)	20	1·024	1130	0·0663	3·74	Vol.
(2)	20	----	----	0·0662	3·74	“
(3)	20	----	----	0·0663	3·74	Grav.
(4)	20	----	----	0·0662	3·74	“
IX (1)	25	1·018	1500	0·0425	2·55	Vol.
(2)	50	----	----	0·0839	2.52	Grav.
(3)	50	----	----	0·0843	2·53	Vol.
(4)	25	----	----	0·0424	2·54	Grav.

potassium. This is particularly true of the blood, where most of the potassium is intimately associated with the protein of the corpuscles. It is necessary therefore to decompose the protein material by oxidation.

The nitric-sulphuric acid mixture was first used for oxidizing the dried blood residue, but was found to work less satisfactorily than in the case of urine. In the ignition of the blood residue oxidized in this way there was apparently a greater tendency to spatter, probably due to the presence of the sulphuric acid. When, however, nitric acid alone was used for the oxidation, there was a tendency for the residue to burn off explosively on ignition. The analytical results from the first specimen given in Table II were obtained by treating weighed portions of defibrinated blood with about 2^{cm^3} of bromine in covered evaporating dishes, allowing them to remain in a warm place under the hood for about one hour. The excess of bromine was then removed over the steam bath, the residue evaporated to dryness, and ignited sufficiently to char the organic matter. The residue was thoroughly extracted with hot water and the extract evaporated off with a few drops of sulphuric acid. The residue was then ignited to remove any ammonium salt which might have escaped the action of the bromine and any organic matter which might have passed through the filter.

The second specimen was a half liter of clotted sheep's blood, from which no homogeneous portions could be taken. The whole mass was, therefore, evaporated over a steam bath and oxidized with concentrated nitric acid, getting everything into solution except a little lipoid material. The solution was made up to the original volume, and aliquots of 25^{cm^3}, representing 30 grm. of blood, were pipetted off. These portions were evaporated to dryness and gently ignited, but not sufficiently to produce explosive decomposition. The residues were then moistened with concentrated sulphuric acid and ignited carefully to remove the organic matter and the ammonium salts. For the results of the second and third divisions of Table II weighed portions of serum and lymph were similarly oxidized with nitric acid and subsequently ignited with a little sulphuric acid. The potassium in all the residues thus obtained was estimated gravimetrically or volumetrically as previously described. The results obtained for potassium in circulating fluids are given in the following table.

C. *Potassium in milk.*

In addition to lactose and the inorganic salts, milk contains a large amount of protein, chiefly casein, and varying amounts of fat. The ease with which casein is precipitated suggested the possibility of making a complete separation of the inorganic salts and casein, but it was found that after thoroughly wash-

TABLE II.

		Nature of fluid	Amount taken	K_2O found		Method
			grm.	grm.	per cent	
I	(1)	Defibrinated	10·89	0·0227	0·21	Grav.
	(2)	pig's blood ..	11·21	0·0228	0·20	Vol.
	(3)	....	20·33	0·0391	0·19	“
	(4)	....	10·16	0·0203	0·21	“
	(5)	....	10·85	0·0211	0·20	“
	(6)	....	11·03	0·0236	0·21	“
II	(1)	Sheep's blood	30·00	0·0174	0·058	Grav.
	(2)	....	30·00	0·0179	0·060	Vol.
	(3)	....	30·00	0·0181	0·060	Grav.
	(4)	....	30·00	0·0181	0·060	Vol.
	(5)	....	30·00	0·0180	0·060	“
III	(1)	Serum of dog's blood ..	10·11	0·0024	0·024	Vol.
	(2)	....	10·04	0·0024	0·024	Grav.
	(3)	....	10·07	0·0023	0·034	Vol.
IV	(1)	Dog's lymph	10·28	0·0018	0.018	Grav.
	(2)	....	10·01	0·0019	0·019	Vol.
	(3)	....	10·00	0·0020	0·020	“
	(4)	....	10·03	0·0019	0·019	“
	(5)	....	10·12	0·0019	0·019	“
	(6)	....	10·32	0·0022	0·021	Grav.

ing the precipitated casein it still contained appreciable amounts of potassium. It was found preferable to evaporate weighed portions of milk to dryness, oxidize with concentrated nitric acid, again evaporate to dryness, and ignite gently until most of the organic matter was burnt off, finishing the ignition after moistening the residue with concentrated sulphuric acid. In the residues thus obtained the potassium was estimated gravimetrically or volumetrically as in the previous work.

The results obtained for potassium in two specimens of cow's milk are given in Table III.

TABLE III.

			Milk taken	K_2O found		Method
			grm.	grm.	per cent	
I	(1)	....	25·8	0·0413	0·16	Vol.
	(2)	....	25·8	0·0432	0·17	“
	(3)	....	25·8	0·0428	0·17	Grav.
	(4)	....	51·6	0·0833	0·16	Vol.
II	(1)	....	25·7	0·0454	0·18	“
	(2)	....	25·7	0·0457	0·18	“
	(3)	....	25·7	0·0451	0·18	Grav.

Summary.

Where protein does not occur in animal fluids it was found most advantageous to oxidize the dried residue with a 9 : 1

nitric-sulphuric acid mixture. In the presence of protein oxidation by bromine, or by nitric acid alone, finishing the ignition in the latter case with a little concentrated sulphuric acid was found more satisfactory.

For the volumetric estimation the ignited residue was treated with a few drops of acetic acid and a little water. To this solution an excess of sodium cobalti-nitrite was added and the mixture evaporated nearly to dryness. The residue was cooled, treated with cold water, filtered on asbestos and well washed with a half saturated sodium chloride solution. The precipitate was oxidized by an excess of hot standard potassium permanganate, the solution bleached by an excess of standard oxalic acid, and titrated to color with permanganate.

For the gravimetric controls the calcium, phosphoric acid and iron (in the case of the blood) were removed either before or after the oxidation and ignition. The residue of sulphates was dissolved in a little hydrochloric acid and water, and the potassium estimated as the chlorplatinate, taking care to wash the precipitate with alcohol, Gladding's reagent and again with alcohol.

Conclusions.

The necessity of allowing the cobalti-nitrite mixture to stand from 12 to 20 hours to complete the precipitation, suggested by Gilbert, Adie and Wood, and others, is avoided by evaporating the mixture nearly to dryness. The removal of the cobalt from the precipitate before oxidation with permanganate is unnecessary, since the cobalt is reduced and not reoxidized in the titration process, and since with proper dilution its color does not interfere with the end point.

For small amounts of potassium fairly accurate results are obtained by using the permanganate factor calculated from Adie and Wood's formula for potassium cobalti-nitrite. Sutton has suggested that more accurate results are secured by obtaining a factor empirically from a pure potassium salt. All the results from this and previous papers were obtained, however, by using the theoretical factor calculated from the formula of Adie and Wood, their analyses of potassium sodium cobalti-nitrite having been verified by the analysis of a carefully prepared salt.

The chief sources of error in the method appear to be in the slight solubility of the potassium sodium cobalti-nitrite, being one part in 25,000 to 30,000 parts of water at room temperature, and its tendency to include traces of sodium cobalti-nitrite. These sources of error tend in opposite directions, resulting usually in a positive error, which by proper washing of the precipitate may be kept within fair limits.

The method requires less time and labor than the chlorplatinate method, and is applicable in the presence of substances which form no insoluble cobalti-nitrites and which neither oxidize oxalic acid nor reduce potassium permanganate.

Art. LIII.—*The Meso-Silurian Deposits of Maryland;* by Wm. F. Prouty.*

The present article discusses briefly the lithological and faunal characteristics of the deposits in the state of Maryland lying between the massive Tuscarora (White Medina) sandstone below and the Salina formation above. These deposits are approximately eight hundred feet in thickness and represent the lower and middle portion of the Meso-Silurian series as shown in western New York. The lower portion corresponds to the pre-Rochester Silurian, the Clinton of common usage, while the upper portion is the approximate equivalent of the Rochester, or the lower division of the Niagara group of common usage.

It is moreover probable that these deposits are equivalent to the typical Clinton of Hall exposed at Clinton, Oneida County, N. Y. The latter, according to both E. O. Ulrich† of the U. S. Geological Survey and to C. A. Hartnagel† of the New York Survey, contains in its upper portion a fauna equivalent to the Rochester or Lower Niagara fauna of western New York. It is very unfortunate that the fauna of the typical Clinton should have gone so long unstudied, thus allowing at the present a double meaning of the term Clinton, as seen below.

The Meso-Silurian deposits of western New York and the interior may be subdivided as follows:

$$\text{Meso-Silurian}\left\{\begin{array}{l}\text{B. Niagara}\left\{\begin{array}{l}\text{3. Guelph}\\ \text{2. Lockport}\\ \text{1. Rochester}\end{array}\right.\\ \\ \text{A. Clinton}\end{array}\right.$$

while the Meso-Silurian deposits of eastern New York, Pennsylvania, Maryland, etc., may be subdivided as follows:

$$\text{Meso-Silurian}\left\{\text{A. Typical Clinton}\left\{\begin{array}{l}\text{2. Rochester of common usage}\\ \text{1. }\textit{Clinton}\text{ of common usage}\end{array}\right.\right.$$

I shall not enter into a discussion of the nomenclature, but shall use the term *Clinton* in the restricted sense to include only the portion below the Rochester.

In the study of the Maryland Meso-Silurian deposits all the important exposures in the state have been visited and at each

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* Published by permission of the Director of the Maryland Geological Survey.

† From letters of recent date.

place careful measured sections and fossil collections have been made. With the exception of the Ostracods and Bryozoa, the fossil study has been practically completed. In the pursuance of his work the author has had access to the collections of the National Museum, the New York Museum of Natural History, the New York State Collection at Albany, and several smaller and private collections. He is also greatly indebted to Prof. Schuchert of Yale University, Dr. E. O. Ulrich of the U. S. Geological Survey, Dr. C. K. Swartz of Johns Hopkins University, and others for assistance. He is further indebted to the Director of the Maryland Geological Survey for the privilege of publishing this article.

Before turning to the present discussion of the Meso-Silurian in Maryland, let us make a brief historical review of what has already been done in this area and what have been and are the views held concerning it.

Historical Review.—Nearly fifty years ago Philip Tyson, the state agricultural chemist of Maryland, published* the first report of importance dealing with the geology of western Maryland. He touched but briefly upon the formations under consideration, using terms, "the Clinton" for the pre-Rochester Meso-Silurian and "the Onondaga" for the remainder of the Meso-Silurian and the Cayugan. In 1874 Prof. James Hall of New York, who had worked in Maryland, especially in the Lower Helderberg, did not recognize the presence of Niagara. It appears that he later did, as he cites *Spirifer crispus* and *Homeospira apriniformis* from the "Niagara" of Maryland.

In 1893 a preliminary geological map† of the state showed the whole Meso-Silurian deposits under the name "Rockwood." James D. Dana‡ in 1895 recognized in Pennsylvania, immediately north of Maryland, a commingling of Clinton and Niagara fossils in the upper Clinton beds, and states that there frequently occur some distance above the top Clinton iron-ore, a succession of thin limestones which in many places contain Niagara fossils.

The author of the Piedmont Folio§ discussed a part of the Maryland area, using the terms Rockwood-(Clinton or pre-Rochester Meso-Silurian) and Lewiston (later Meso-Silurian, Cayugan and Lower Helderberg). There is here a preliminary discussion of the two formations as Rockwood and the lower part of the Lewiston.

The first detailed lithological study, however, of the Meso-

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* Geological Map and Report, 1861.

† Map to accompany "Maryland: Its Resources, Industries, and Institutions." G. H. Williams and W. B. Clark.

‡ Manual, 4th edition, 1895.

§ Geol. Survey Atlas, Folio No. 28, 1896.

Silurian of Maryland was made in 1900 by C. C. O'Harra.* He used the terms Clinton and Niagara, correlating the formations in Maryland with those in western New York.

It has long been known by all geologists working in the Appalachian districts that there is a marked stratigraphic change as one passes westward over the protaxis of these mountains. For the explanation of this fact the theory of a profound fault was suggested by some but accepted by few. Sir William Logan of the Canadian Survey, in 1866, suggested the possible existence of a narrow basin of deposition west of the protaxis to account for the stratigraphic break.

It has also long been recognized that there exists a faunal difference in some of the deposits west of the protaxis in the Appalachians and in those west of the Allegany Mountains in New York and the interior. The explanation of this fact was little dwelt upon until recently, when E. O. Ulrich and Charles Schuchert, after careful investigation and faunal study, put forward a most admirably developed theory† to account for the apparent condition. They conclude from paleontological evidence that there existed a barrier of great length, which separated from the interior sea a long and narrow body of water lying in the Appalachian region, the "Cumberland basin," in which sediments were deposited bearing fauna more closely related to the east Canada and European deposits than to those of the interior sea; that the Atlantic crossed over the barrier forming the eastern side of this basin in about Beekmantown time, but was restrained by the western barrier of this basin from mingling with the interior sea, possibly from Clinton but certainly from Niagara time well into Oriskany time. The barrier forming the western side of the Cumberland Basin extended, according to Ulrich and Schuchert, from the region of Cayuga Lake, N. Y., southward to west of Altoona, Pa., thence parallel to the trend of the Appalachian Mountains through central West Virginia into eastern Tennessee. In discussing the fauna of the Cumberland Basin, Ulrich and Schuchert state that few species are identical with those of the interior sea, and that the earlier fauna recalls the Clinton, while it passes above into one which may be compared to the Niagara.

Charles Schuchert, in a later publication,‡ speaking of the Maryland deposits which include the Clinton and Niagara, says that save *Atrypa reticularis* and *Leptaena rhomboidalis* all the species appear to be new. Further, he directs attention to the absence of such characteristic forms of the western or

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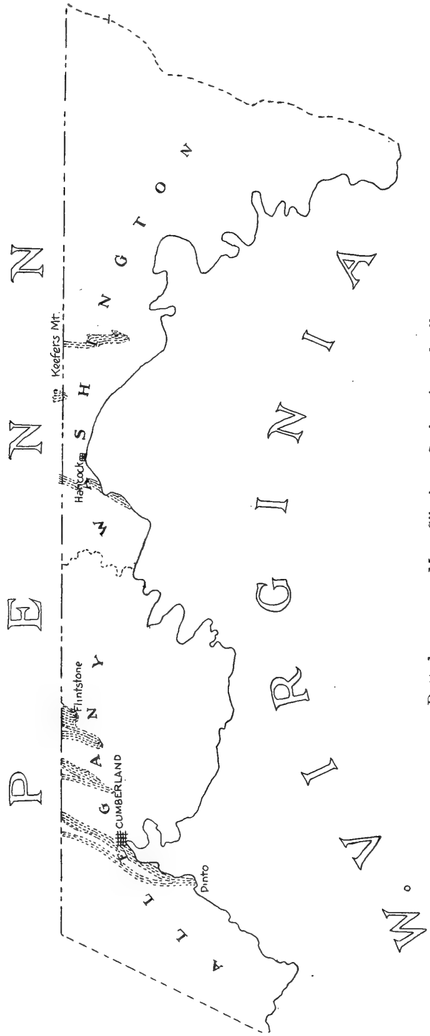
* The Geology of Allegany Co., Md.; Md. Geol. Survey Rept., pp. 57-164, 1900.

† Paleozoic Seas and Barriers in Eastern North America. N. Y. State Mus. Bul. No. 52, 1902.

‡ Lower Devonic and Ontario Formations of Maryland, 1903.

Mississippian sea as *Spirfer radiatus*, *Spirifer Niagarensis*, *Spirifer Crispus*, *Spirifer sulcatus*, *Pentamerus oblongus*, *Caryocrinus*, and *Eucalyptocrinus*. Of these, *Spirifer radiatus* and *Spirifer crispus* are now known to occur in the Cumberland Basin.

FIG. 1.



Dotted areas are Meso-Silurian. Scale 1 in.=16 miles.

Mr. C. A. Hartnagel of New York, in an article* in 1902, shows, however, that the western or Helderbergian barrier was not continuously and completely effective from Clinton to Oriskany time, since the mingling of Guelph and Cobleskill fauna evidence the crossing of the barrier during Cobleskill time.

Up to the present less than half a dozen species of fossils have been definitely described from the Maryland, Clinton, and later Meso-Silurian.

General Description.—The outcrop of the Meso-Silurian rock in Maryland is limited entirely to the region of the Alleghany Ridges proper, in Washington and Allegany Counties. The area covered is about twenty-four square miles, of which the Clinton occupies fifteen and the Later Meso-Silurian about nine. As would be expected from the general Appalachian structure, the rocks under discussion flank anticlinal folds which

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* Preliminary Observations on the Cobleskill Limestone of New York. Rept. N. Y. State Paleont. for 1902, p. 1156.

have a general trend N. 20°–30° E. There are six such folds exposing these strata in Maryland: three in Allegany County and three in Washington County (see map, fig. 1). The axes of the anticlines are formed by the very resistant "Tuscarora" or "white Medina" sandstone. Nearly all the folds are unsymmetrical, giving a much narrower outcrop on the west than on the east side.

General Character of the Deposits.

Clinton Formation.

The rocks of this age in Maryland consist essentially of reddish and olive to grayish and brown argillaceous shales which are slightly lighter in color and less fossiliferous toward the bottom. The exposed surfaces of this shale often show a deep scarlet color. Thin sandstone bands occur at irregular intervals throughout nearly the whole formation and become more numerous toward the bottom, giving the formation the appearance of grading into the Tuscarora quartzite. These thin sandstone bands were in general originally more calcareous than at present and are uniformly more fossiliferous than the shale in which they occur. Toward the top of the formation limestone bands become numerous and replace the sandstone layers. They seldom exceed six inches in thickness, and in some localities are very fossilferous. Immediately overlying the limestone-bearing shales throughout the region there occurs a quartzitic sandstone, of variable thickness, which in character resembles very closely the Tuscarora. This sandstone thickens markedly toward the east, increasing from ten feet in thickness near Cumberland to nearly seventy feet in some eastern exposures. In the top portion of this sandstone is found the so-called top Clinton iron-ore, usually not more than a foot in thickness and commonly of too low a grade to work. In places, however, it is thicker and has been enriched so that in the past it has served as an ore and might at present locally be so called were it more accessible to the railroad. In this latter respect the top Clinton ore differs markedly from the so-called bottom Clinton ore which occurs throughout the Maryland area from one hundred and twenty to one hundred and sixty feet from the bottom of the formation and which, though it sometimes attains forty feet in thickness, is not sufficiently high in iron to be valuable as an ore. This lower *iron sandstone* occurs in two beds separated by from six inches to six feet of olive shale. Both the bottom and top "ore" bodies contain numerous though very poorly preserved fossils.

The olive shales and thin crystalline limestone bands immediately above the top Clinton iron-ore sandstone contain a greater percentage of Rochester fossils than of those of the pre-Rochester Meso-Silurian, and consequently it would appear that the lower limit of the Rochester should be drawn at the top of the heavy sandstone layer. The thickness of the Clinton does not vary far from five hundred and fifty feet.

The Later Meso-Silurian (*Rochester*).

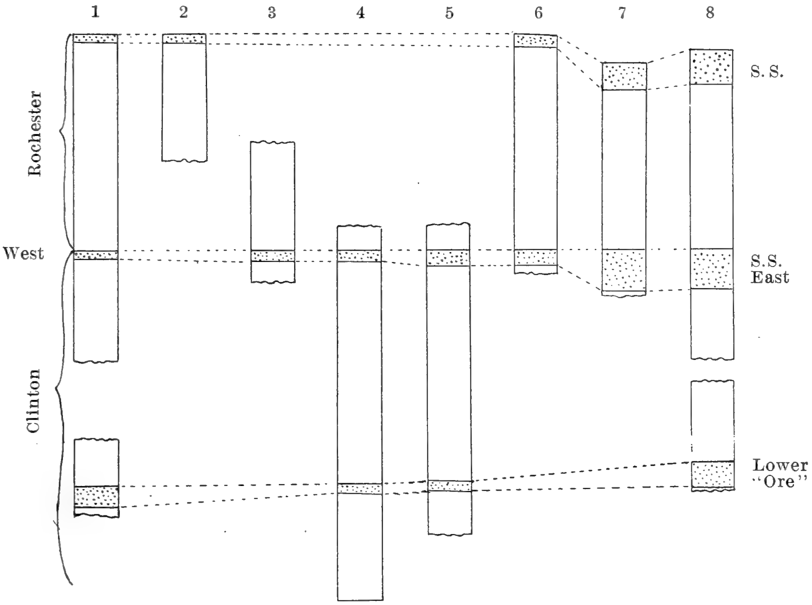
The rocks of the Later Meso-Silurian formation, as herein discussed, include those lying between the heavy band of sandstone bearing the top Clinton iron-ore and the bed of disintegrated yellow rock full of *Leperditia* which marks the base of the overlying Cayugan, and are composed for the most part of thin-bedded limestones with shale partings. For a short distance above the bottom and for a greater thickness near the top the shales increase and preponderate over the limestone. The lowest limestone layers are grayish blue in color and, together with the shales which immediately overlie the Clinton sandstone layer, are very fossiliferous. The upper limestones are uniformly of a darker color and more compact, sometimes occurring in more or less lenticular beds with thin shale partings. In general the middle limestones and shales contain few fossils, with the exception of Ostracods and a few Favosites and Orthoceras. Toward the top, however, the brachiopod life begins again to abound and some beds are very fossiliferous. The upper shales are usually darker in color than those below and often become arenaceous, bearing thin sandstone lenses, while the top of the formation is often formed by a bed of sandstone of variable thickness which is often very ferruginous. These upper dark shales usually carry a great number of Ostracods and poorly preserved Bryozoa.

Going toward the east, one generally finds that both the lower shales and the upper ferruginous sandstone layers increase in thickness. The thickness of the formation is in general not far from three hundred feet. At Pinto, where the most accurate measurements were made, though they are not entirely satisfactory because of some faulting, these rocks show a thickness of two hundred and eighty-eight feet.

General Lithological Relations.

It is concluded from a comparative study of the different exposures in the state that during the deposition of these sediments there existed a shore line not far to the east, and a gradual deepening of the waters toward the west as far as the section exposed at Pinto (see section, fig. 2 and map, fig. 1). The main facts supporting this conclusion are: the top Clinton sandstone increases gradually in thickness from seven feet at Pinto to some sixty-five or seventy feet in the eastern exposures; the bottom Rochester shales increase in thickness and the bottom limestones consequently decrease in thickness in passing from west to east; the top Rochester sandstone, like the top Clinton sandstone, thickens from eight feet at Pinto to some fifty feet or more in the eastern exposures. If we assume then that the Maryland Meso-Silurian deposits were laid down in a narrow basin of deposition, then Pinto must be east of the central axis of the basin or else the western shore line of this narrow sea must have been much lower than the eastern land was. It is not improbable that both these conditions were true.

Fig. 2.



1. Pinto Section.
2. Cedar Cliff "
3. Rose Hill "
4. Cumberland Section.
5. Six-mile-house "
6. Flintstone "
7. Great Cacapon Section.
8. Keefers Mt. "

Fossil Zones.

In Clinton.—

The Clinton formation, so far as studied, has not shown any well-marked continuous fossil zones. Portions of the strata are much more fossiliferous, however, than others, and the formation as a whole is naturally divisible into four parts:

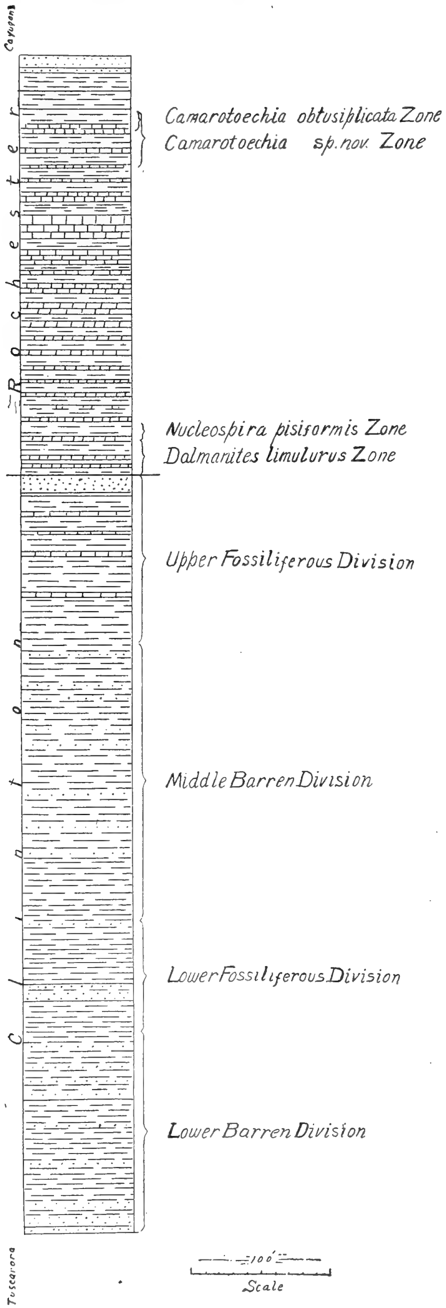


FIG. 3.

(1) a lower relatively barren division including the shales and sandstones up to within some thirty feet of the lower "iron ore," which bears locally at its base a few plant remains, the ostracod *Berichia lata* and the brachiopod *Anoplotheca hemispherica;* (2) a lower fossiliferous division, including the remaining shales below the bottom "iron ore," the ore bed and some fifty to eighty feet of the overlying shales and sandstones; (3) a middle barren division, including some two hundred feet of relatively barren shales and sandstones; and (4) an upper fossiliferous division, including about one hundred feet of shales and interbedded sandstones, replaced by thin-bedded limestone toward the top, about which occurs the very slightly fossiliferous top Clinton sandstone (see sect. fig. 3).

Of the two fossiliferous divisions, the lower is characterized by a large number of tentaculites and ostracods and two species of trilobites. The upper fossiliferous division, on the other hand, is characterized by its branchiopod fauna.

The forms noted in the two fossiliferous divisions are as follows:

From the lower fossiliferous division:

Buthotrephis gracilis var. *intermedia* Hall
**Anoplotheca hemispherica* (Sowerby)
Stropheodonta corrugata (Conrad)
† *Tentaculites* sp.
Clidophorus sp.
* *Calymene blumenbachii*
* *Calymene* sp. nov.
* *Ostracods*

From upper fossiliferous division:

† *Atrypa reticularis* (Linnaeus)
* *Leptaena rhomboidalis* (Wilckens)
Camarotoechia neglecta Hall
* *Chonetes cornutus* (Hall)
* *Chonetes novascoticus* (Hall)
* *Chonetes tenuistriatus* Hall
Spirifer radiatus (Sowerby)
Bucanella trilobata (Conrad)
Calymene clintoni (Vanuxem)

In Upper Meso-Silurian.—

While the Clinton fossils seem to have a rather extended range vertically and a more or less local distribution, making a close zonal study of this formation seemingly impracticable, the overlying Meso-Silurian may be divided into five portions, three of which are well-marked faunal zones. Immediately overlying the top Clinton sandstone and extending vertically sometimes 30 feet, though usually more restricted, is a very prolific faunule, marking a zone called from one of its most widespread and characteristic fossils, the *Dalmanites limulurus zone.* This zone includes more than one-half of the species described from the whole Meso-Silurian series of Maryland. At Cumberland, where this zone was most studied, the following species were observed:

Fauna of the Dalmanites limulurus Zone.

Anoplotheca hemispherica (Sowerby)
* *Atrypa reticularis* (Linnaeus)
Camarotoechia neglecta Hall
Dalmanella elegantula (Dalman)
† *Dalmanella elegantula* var. nov.
* *Leptaena rhomboidalis* (Wilckens)
Reticularis bicostata var. nov.

* Abundant. † Very abundant.

* *Rhipidomella subcirculus* (Simpson)
Rhipidomella hybrida (Sowerby)
† *Rhynchonella* (*tennesseensis*) ? Roemer
Schuchertella supblana (Conrad)
Schuchertella tenuis Hall
Spirifer crispus (Hisinger)
Stropheodonta corrugata (Conrad)
Stropheodonta corrugata var. *pleuristriata* (Foerste)
Stropheodonta sp. nov.
Stropheodonta sp. nov.
Ctenodonta sp. nov.
Pterinea emacerata (Conrad)
Bucanella trilobata (Conrad)
Conularia sp.
* *Diaphorostoma niagarensis* Hall
Platyceras sp. nov.
Platyceras niagarense Hall
Trochoceras sp.
† *Dalmanites limulurus* (Green)
* *Homalonotus delphinocephalus* (Green)
Cornulites sp. nov.

Immediately overlying the *Dalmanites limulurus* zone there is a fossiliferous horizon of some 3 to 15 feet in width, which contains great numbers of *Nucleospira pisiformis* and sometimes a few *Schuchertella* sp. nov. This *Nucleospira pisiformis* zone, which occurs in the calcareous shale and limestone layers, is overlain by some 150 feet of limestone and shales in which the fossils are fewer and more scattered.

This latter division has given us the following species:

Buthotrephis gracilis var. *intermedia* Hall
* *Favosites niagarensis* Hall
Camarotoechia neglecta Hall
* *Homeospira evax* var. nov.
Lingula sp. nov.
Orbiculoidea sp. nov.
Clidophorus sp. nov.
Hormatoma sp. nov.
† *Hormatoma* sp. nov.

Near the top of the formation and usually between 50 and 80 feet below the "disintegrated yellow rock" of the Salina (the Niagara-Salina line) there occurs a band some 30 feet in thickness which is here called the *Camarotoechia* sp. nov. zone. It has yielded the following species:

† *Camarotoechia* sp. nov.
† *Camarotoechia obtusiplicata* Hall
Camarotoechia neglecta Hall
Lingula lamellata Hall
Spirifer sp. nov.
Clidophorus sp. nov.
Cuneamra sp. nov.

* Abundant. † Very abundant.

Above the preceding there is a zone two feet in thickness in which occur great numbers of *Camarotoechia obtusiplicata* mingled with *C.* sp. nov. and *Cuneamra* sp. nov.

The uppermost 50 feet of the Meso-Silurian rocks are in general largely shale and sandstone. They contain very abundant Ostracods and poorly-preserved Bryozoa and, in addition, so far as studied, only two fossils:

Homeospira evax var. nov.
Ctenodonta sp. nov.

Table Showing Number, General Relation and Affinities of Maryland Meso-Silurian Fossils.

Number of forms studied:	
Number of species and varieties studied	56
Number of species previously described	32
Number of new species	20
Number of new varieties	4
Percentage of new forms	
Percentage of new species	35·7
Percentage of new varieties	7·1
Percentage of new species and new varieties	42·8
Occurrence elsewhere:	
Number of species occurring in Arisaig	10
“ “ “ English Silurian	8
“ “ “ Anticosti	5
“ “ “ Ohio Clinton	1
“ “ “ “ Niagara	15
“ “ “ Indiana “	16
“ “ “ “ Clinton	1
“ “ “ New York Rochester	12
“ “ “ New York Lockport	3
“ “ “ Rochester and Lockport	2
“ “ “ Niagara and not referred to either Rochester or Lockport	3

One-fourth (8) of all the previously described species occur in the European deposits, of which species seven are also found in the middle United States.

Number of different species cited from either Anticosti, Arisaig or English deposits	18
Number of these cited from either Indiana or Ohio	12

From a study of the foregoing fossil lists and the above table one is impressed with the marked faunal difference between the Meso-Silurian deposits of Maryland and those of Western New York and the interior. The fact that there are so many new species (42 per cent of all studied) argues very strongly in favor of the supposition that the Maryland Meso-Silurian deposits were laid down in a sea distinct from that of Western New York and the interior. This argument is further strengthened by the fact that several of the most prominent species of the interior Meso-Silurian sea are not represented in Maryland. That there were short periods, however, when the low barrier separating this Cumberland Gulf from the interior epicontinental sea was ineffective, is shown by a few zones in the Maryland Meso-Silurian which have a prolific development of certain of the more important Western New York forms, as for instance the *Dalmanites limulurus* zone, the *Nucleospira pisiformis* zone and the *Camarotoechia obtusiplicata* zone. (See fig. 3.)

The great coral development of the western upper Niagara is entirely lacking in the Maryland deposits. In fact there are practically no fossils which belong distinctively to the Lockport or Guelph formation, and it is probable that during the greater part of these two periods there was little or no sedimentation in the Maryland area. The Meso-Silurian sea may have continued to exist in the Cumberland Gulf in early Lockport time, but if so, seemingly for a short period only.

It is further interesting to note that one fourth of all the previously described forms are of world-wide distribution; that six of the old forms are characteristic of the deposits of Anticosti, Arisaig or the English Silurian, while fourteen are characteristic of the western interior. This last result is, however, of little value in showing the relative ease of communication between the Cumberland basin and the epicontinental sea to the west and the Canadian deposits to the north and east, since the Canadian deposits have not been studied as well as have those of the interior United States.

Summary.

The Meso-Silurian deposits of Maryland, lying between the Tuscarora and the Salina formation, are about 800′ in thickness and are composed for the most part of shales and thin-bedded sandstones below and of shales and limestone above. This series can be divided into two formations, corresponding in time approximately to the Clinton, accorded to the common usage, and the Rochester of New York. They are, moreover, taken together, the probable equivalent of Hall's typical Clinton as represented at Clinton, Oneida Co., N. Y.

These Meso-Silurian rocks outcrop in the western part of Maryland in Allegany and Washington Counties in six anticlinal folds with typical Appalachian structure. The thickening of the coarser sediments from the western to the eastern exposures indicate the proximity of a shore line toward the east. That a shore line or barrier existed not far to the west of the exposed Maryland Meso-Silurian deposits is not evidenced by a lithogical study, but is sufficiently indicated by the fossil study. This barrier must, however, have been low and at periods ineffective, especially during Rochester time, when, to a greater extent than in the Clinton, well marked fossil zones appear, making a prolific development of some of the more important species of western New York.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *Rate of Production of Helium from Radium.*—Sir James Dewar having succeeded, by the use of the radiometer, in detecting a gas pressure of the fifty-millionth of an atmosphere, and having definitely detected by this means the helium produced in a few hours from about ten milligrams of radium bromide, has undertaken the direct measurement of the helium produced by radium. For this purpose he employed 70 mg. of radium bromide belonging to the Royal Society, which had been used by Dr. Thorpe in his recent determination of the atomic weight of radium. The apparatus employed for measuring the helium consisted of a McCleod gauge in which no rubber joints were used, together with ingenious arrangements for exhausting the apparatus. Any traces of adventitious gases were absorbed by an attached bulb containing charcoal and cooled in liquid air. In one instance the pressure registered at the start of the experiment was 0·000044 mm. The radium salt was occasionally heated and the pressure of the helium was determined from time to time. A steadily maintained helium increment was obtained of approximately 0·37 cu. mm. per gram of radium per day. This result agrees very closely with Rutherford's theoretical calculation, which gives about 0·3 cubic millimeters per day.—*Advance sheets from author.* H. L. W.

2. *Radium in Tufa Deposits.*—Schlundt has examined a number of these deposits from Hot Springs, Ark., and finds that the amount of radium in them varies to a remarkable degree. Some of the samples gave low results corresponding to 0·56, 0·72, 0·73, 1·18, 2·62 and 2·85 $\times 10^{-12}$ g. of radium per gram of tufa, while other samples gave such results as 26·7, 36·3, 156·0, 227, 1322 and 1900 $\times 10^{-12}$ g. of radium. These deposits appear to be derived from springs of similar character, and differences in the physical character of the material gave no clue to their radium contents. Boltwood had previously found considerable variations in the radium in the water from different springs in this locality, and it appears from a limited correlation of the results that no correspondence exists between the radium contents of the waters and of the tufas deposited by them.—*Chem. News,* xcviii, 199. H. L. W.

3. *A Compound of Cobalt with Carbon Monoxide.*—Mond, Hirtz and Cowap have succeeded in preparing cobalt carbonyl, $Co(CO)_4$, which corresponds in composition to the remarkable nickel compound described by Mond and other co-workers in 1890. The cobalt compound was prepared by taking advantage of a method of Dewar for facilitating the formation of nickel

carbonyl, which consists in using carbon monoxide under pressure at a correspondingly higher temperature. A pressure of 100 atmospheres was used for the carbon monoxide, and under this condition a combination with finely divided metallic cobalt took place between 150 and 200° C. The cobalt carbonyl is a very volatile substance which condenses in the form of large orange crystals when the vapor is cooled by ice. The compound is very unstable, melting with decomposition at about 42 to 46° C. It is gradually decomposed in air, yielding a deep violet substance which has not yet been investigated.—*Chem. News*, xcviii, 165. H. L. W.

4. *Cyanide Processes;* by E. B. WILSON. 12mo, pp. 249. New York, 1908 (John Wiley & Sons).—This is the fourth edition, revised and enlarged, of a well-known treatise. Owing to the recent improvements in cyanide practice, especially in the treatment of slimes, the author has added a chapter giving the latest methods for treating such material. The book, as has been the case with previous editions, deals with the theories and facts connected with the processes, without giving details of the construction of the plant and machinery. H. L. W.

5. *Magnetic Rotation of Electric Discharge.*—Professor D. N. MALLIK has studied the old experiment of De La Rive, which consists in causing the rotation of an electrified discharge around the pole of a magnet, and classifies three stages: showery, band, and glow. The discharge rotates under the influence of the magnetic field, only when it is in the form of a band over a range of pressure depending on the nature of the gas or vapor in the tube through which the discharge passes, the E. M. F. producing the discharge and the distance between the electrodes. In air, and probably in all gases, the angular velocity of rotation is proportional to the E. M. F. producing the discharge, and increases as the spark length decreases. Professor Mallik also analyzes the conditions of pressure and temperature.—*Phil. Mag.*, Oct., 1908, pp. 531–550. J. T.

6. *A Directive System of Wireless Telegraphy.*—E. BELLINI and A. TOSI describe such a system which depends upon a method of orienting the sending coils of a transformer with respect to the antennæ. They give a test of their method, carried out between the stations of Dieppe and Havre. On turning what they term their radiogiometer in the direction of Havre, reception of messages was effected. On turning the pointer of this instrument to 180° this reception ceased entirely. The authors point out the strategical advantage of their system.—*Phil. Mag.*, Oct., 1908, pp. 638–657. J. T.

7. *Positive Rays.*—Professor J. J. THOMSON, in an extended article on this subject, reviews and corroborates the results of Villard (Comptes Rendus, cxliii, p. 673, 1906) on what is termed retrograde rays: that is, positive rays which proceed from the cathode and travel against the positive rays, proceeding from the anode. Professor Thomson also gives a theory of the method by means of which these retrograde rays obtain their velocity. The

paper also contains a discussion of the nature of positive ions in different gases, when the ionization has settled into a steady state.—*Phil. Mag.*, Oct., 1908, pp. 657–691. J. T.

8. *Amount of Radium Emanation in the Atmosphere near the Earth's Surface.*—Experiments on this subject have been carried out by Professor Eve at McGill University, Montreal, in a room fifty feet above the ground. The outside air was drawn through cotton wool; then through three glass tubes containing cocoanut-shell charcoal. The air currents were continued for 2·7 days, at a speed of 6·7 cm^3/sec. The tubes were then heated over Bunsen burners, so that the gases absorbed by the charcoal were expelled and collected over water and then examined in the usual way, by means of an electroscope. It was found that the amount of radium which would be in equilibrium with the average amount of radium emanation in a cubic meter of air at Montreal measured at intervals 1907–8 is 60×10^{-12} gram. This amount varied with cyclonic and anticyclonic conditions—but not appreciably from summer to winter.—*Phil. Mag.*, Oct., 1908, pp. 622–632. J. T.

9. *Absorption of Röntgen Rays.*—Dr. Adams, working in the Jefferson Physical Laboratory, measured the absorption of these rays through various substances (this Journal, xxiii, Feb., 1907; also Proc. Am. Acad., xlii, No. 26). W. Seitz, in a preliminary paper, undertakes the same subject with the modification of using an aluminium window in the X-ray tube, to diminish as much as possible the sifting of the rays due to glass walls.—*Ann. der Physik.*, No. 12, 1908, pp. 301–310. J. T.

10. *The Zeeman Effect in Solar Vortices.*—The announcement of the discovery of this effect by Professor George A. Hale of Mt. Wilson Observatory has led to interesting discussions in Nature, Oct. 8 and Oct. 29, 1908. J. T.

11. *The Study of Stellar Evolution, an Account of some Recent Methods of Astrophysical Research;* by George E. Hale. Pp. xi + 252, with 104 plates. Chicago, 1908. Decennial Publications of the University of Chicago, Second Series, Vol. X.—The study of solar physics is a territory which resembles Central Africa,—many men have visited it and have picked up treasures here and there, but almost no systematic attempt has been made until the last few years to unravel its mysteries and to introduce order into the chaos of isolated facts and theories which have been gathered in the general store of knowledge. As is generally known, Professor Hale has embarked on such a venture at Kenwood, at the Yerkes Observatory, and for the last three years at Mount Wilson under the auspices of the Carnegie Institution. With a multitude of problems under investigation, it is too early yet to expect very extensive results: the facts have still to be obtained.

The volume under review may be classed as a sort of traveller's guide, showing the roads which have already been opened, the methods used for continuing the exploration and the theories which indicate directions for future work. Its plan is best described in the author's own words: "I finally adopted the plan of describing a connected series of investigations, laying special stress on the observational methods employed, in the hope of explaining clearly how the problem of stellar evolution is studied. . . . The various researches described are chosen rather arbitrarily, in some cases with more regard for my personal acquaintance with the facts than because of their intrinsic importance."

While the main problem is that given in the title, the greater part of Professor Hale's latest book has been directed towards the sun. He has shown not a little ingenuity in devising and constructing instruments for the observation of a body which gives us so much heat that accurate work is seriously interfered with by the distortion of the lenses and mirrors employed. These devices, old and new, are described in nearly half of the printed matter of the volume with the reasons which have led to their adoption. Interspersed are chapters on the hypotheses which it is desired to test. The author has also considered those who have only a general acquaintance with scientific methods, and he outlines briefly the main principles of his subject,—spectrum analysis, evolution of a star, the construction of a telescope, and so on.

In such a volume, criticism of details is unnecessary especially when so many of the questions at issue are still sub judice. It is to be recommended to those who wish to know the facts and problems set forth in an attractive manner; parts of it will appeal to the trained student desiring a brief account of the latest developments; and perhaps more than all, the suggestiveness which characterizes Professor Hale's work will be welcome to those who are looking for problems to solve. To mention only a single instance of the latter, we have yet to find out how to make a quantitative estimation of time changes on the solar surface with some approach to accuracy.

About half the thickness of the volume is taken up with excellent photographs, and the somewhat rambling order in which the various subjects are treated will not be found an objection if full use is made of the index. The latter would have been more conveniently placed at the end instead of the middle just before the plates, which are placed together in the second half of the book.

ERNEST W. BROWN.

12. *Die Korpuskulartheorie der Materie;* von Dr. J. J. THOMSON, Autorisierte Übersetzung von G. SIEBERT. Pp. vii+166. Braunschweig, 1908 (F. Vieweg & Sohn).—This is the German translation of Professor Thomson's latest book, which is an amplification of a course of lectures given in 1906 at the Royal Institution. It is similar in character to the author's Silliman Lectures, "Electricity and Matter," delivered at New Haven in 1903, and is essentially a sequel to them; the rapid progress in the development of the electrical theory of matter is strikingly illustrated by a comparison of the two books. The first three chapters give a brief account of the properties of the electron or

corpuscle as determined experimentally and as deduced from electrical theory. The fourth chapter is concerned with that theory of metallic conduction which is based upon the assumption that the current is carried by free electrons. Although this theory is very successful in explaining most of the facts of metallic conduction, there are difficulties in connection with it which have led Professor Thomson to bring forward another theory, not quite so simple and perspicuous as the first, but free from some of its troubles; this theory is the subject of the fifth chapter. The sixth chapter gives an account of the author's remarkable speculations with regard to the structure of the atom, in which it is shown that a purely electrical model can account for many of the chemical properties of atoms and in particular for the valence relations of the periodic system. The seventh and final chapter deals with the considerations which have recently led the author to reduce his estimate of the number of corpuscles in the atom from many thousands to a number approximately equal to the atomic weight; and the chapter closes with an ingenious attempt to account for the mass of the atom in terms of the ether, but on quite different lines from the electrodynamic explanation of the mass of the electron. H. A. B.

13. *Magneto- und Electro-Optik;* von Dr. WALDEMAR VOIGT. Pp. xix + 396. Leipzig, 1908 (B. G. Teubner).—The effects produced by magnetic and electric fields upon the optical properties of bodies have been recognized as of great importance to the theory of the ether, ever since the original discovery of the Faraday Effect. They have, however, proved very difficult to deal with either experimentally or mathematically, and not very much real progress was made until the discovery of the Zeeman Effect in 1896. This led to a great number of very interesting and significant experimental investigations; and the application of the electrical theory of light to these observations has resulted in a very important body of theoretical knowledge which is not yet as familiarly known by most physicists as it should be. The present book by Professor Voigt, to whom we owe many important contributions to the mathematical side of this subject, will enable us to acquire this knowledge far more easily and satisfactorily than has been possible hitherto. Successive chapters deal with the Faraday Effect, the Zeeman Effect, the connection between the two, the effects observed in absorbing crystals by Jean Becquerel, and the two Kerr Effects. Experimental methods and results are described and illustrated by excellent reproductions of photographic spectra; and the theory of these phenomena is developed to a greater extent, probably, than it has reached in the hands of any other writer. Some parts of the book are unquestionably difficult, but the subject of which it treats is not an easy one. H. A. B.

14. *The Evolution of Forces;* by Dr. GUSTAVE LE BON. Pp. xv + 388. New York, 1908 (D. Appleton & Co. The International Scientific Series).—The author of the present work is well known

as one of those workers in the fields of science who are unappreciated by their contemporaries, and who labor under the delusion that a conspiracy against them exists among the representatives of "official science." An account is given of his theories and discoveries and the way in which they have been first neglected by others and later appropriated without his receiving credit. The book belongs to a class which is not unknown in the history of science. H. A. B.

15. *Experimental Electricity;* by G. F. C. SEARLE. Pp. xvi + 183. Cambridge, 1908 (University Press).—Mr. Searle's unusual ability as a teacher of laboratory physics has long been recognized by those who have known of his work at Cambridge, or who have used the simple and accurate apparatus which he has designed. A series of laboratory manuals from his pen will undoubtedly be of service to teachers, and one is glad to learn from the preface that the present volume is to be followed shortly by another on Experimental Optics, and that volumes are planned, to deal with Mechanics, Electricity and Magnetism, and Heat and Sound. H. A. B.

16. *The New Physics and its Evolution;* by LUCIEN POINCARÉ. Pp. xv + 344. New York, 1908 (D. Appleton & Co. International Scientific Series). — This is an unusually good presentation of the recent progress in physics, and of the connection between modern theories and those of an earlier date. Although it is necessarily much condensed, it betrays few of the ordinary faults of condensation; one paragraph follows another smoothly and logically without appearance of haste, and with the clearness that is characteristic of French writers. The knowledge of the author is obviously very extensive and nearly always accurate, and his appreciation of historical perspective is admirable. The translation, however, is not above criticism. French phrases are often translated literally with amusing results, as on p. 192, where the *Reststrahlen* of Rubens and Nichols are spoken of as "the waves which remain." The notes by the editor of the English version are by no means up to the standard of the text. They are sometimes entirely wrong, as on pages 24 and 178; others give a quite erroneous impression as to the significance of the facts stated, as on pp. 172 and 311. These are, however, small defects in a very good book, and the author is evidently not responsible for them. H. A. B.

17. *The Principles of Mechanics;* by HENRY CREW. Pp. x + 295, with 110 figures. New York, 1908 (Longmans, Green & Co.).—This text-book is especially intended for students of physics and engineering, who have had a first-year course in physics and in the elements of the calculus. Like Professor Crew's other text-books, it is admirably adapted to the use for which it is designed. It is simple, straightforward and logical, but without making a fetich of logic; and the student is kept in close touch with the realities of the laboratory and of ordinary life. The constant use of the useful analogy between problems of translation and of

rotation is a conspicuous feature of the book and will earn the approval of every experienced teacher. It may be a question whether it is not preferable to allow the student to gain first some idea of the dynamics of a particle, and to build upon this the dynamics of rigid bodies, instead of introducing them side-by-side as is done in this book and afterward developing their relations. Some teachers also will regret that the use of the principle of energy is so long delayed. These are, after all, questions of taste and not very important. Taken as a whole, the book is so good and so well suited to its purpose, that one may venture to predict for it a very considerable and well-deserved popularity.

H. A. B.

II. Geology and Mineralogy.

1. *West Virginia Geological Survey.* Volume II (A). *Supplementary Coal Report;* by I. C. White, State Geologist. Pp. xiv, 720, with map in pocket. Morgantown, 1908.—In 1903 the second volume of the West Virginia Geological Survey was published, giving an account of the coals of the northern part of the state, with also notes in regard to those of the southwestern portion. The present volume, IIA, discusses in all fulness of detail the Great Kanawha and New River coal fields, and those lying between them and the Kentucky line. The two volumes together, therefore, present an exhaustive account of the resources of the state in respect to this important industry. It may be noted that in 1907 some 48,000,000 short tons were produced, and the increase in rate of production at present averages nearly 4,000,000 tons per year. A careful survey of the entire state leads to the conclusion that it may be expected to yield somewhere between fifty and sixty billion short tons of commercial coal, and about one-third as much more of impure and bony coal available for the gas engine. Most of the coal now marketed ranks high in calorific value, and some of it is not exceeded by that of any other bituminous coal fields in the world.

A large map of the state on the scale of seven miles to the inch has been distributed with this volume. It shows the distribution of the several coal formations and also the areas of oil, gas and limestone, with the principal anticlinal lines.

2. *Florida State Geological Survey,* E. H. Sellards, State Geologist. First Annual Report 1907–8. Pp. 114, with 6 plates. Bulletin No. 1. A Preliminary Report of the Underground Water Supply of Central Florida. Pp. 103, with 6 plates and 6 figures. Tallahassee, 1908 (Capital Publishing Co.).—The first annual report of the Geological Survey of Florida contains the administrative report for 1907–8, by the state geologist, Prof. E. H. Sellards, with a sketch of the geology of the state. An account is also given of the mineral industries, chief of which is the phos-

phate mining, the annual value of which now exceeds $6,000,000. Since the beginning of active mining in 1888, to the end of 1907, some 12,000,000 tons, valued at $48,000,000, have been taken from the Florida phosphate fields. There is also included a bibliography of Florida geology.

Bulletin No. 1 discusses the underground water supply of the central portion of the state. The facts are interesting, as the conditions are peculiar in various directions. The large annual rainfall taken in by the limestone rocks yields springs notable for their number and their unusual size. The basin of Silver Spring, for example, has a depth of 30 to 36 feet, and the total flow from several vents is not less than 369,000 gallons per minute. It is shown that the springs doubtless receive their water supply from the rainfall of the immediately surrounding country. There are two principal areas of artesian wells; one on the east coast, and the other on the southern Gulf coast. The conditions in central Florida are not favorable for flowing wells.

This bulletin will be of great value to the people of the state, and to geologists in general it is interesting on account of the descriptions of the underground water supplies in cavernous limestone. The State Geologist reports that the Survey work will be carried on particularly on economic lines, but that maps are also under preparation and arrangements have been made with the United States Geological Survey for a joint study of the larger field problems. He is to be congratulated on the character of his first year's work. H. E. G.

3. *Wisconsin Geological and Natural History Survey;* E. A. Birge, Director. Bulletin No. XX. Economics Series, No. 13. The Water Powers of Wisconsin; by Leonard S. Smith. Pp. xviii, 352, with 54 plates and 17 figures. Madison, 1908.—The state of Wisconsin is unusually rich in its water power resources; not more than half a dozen other states in the country being so well situated. As at present developed it is estimated that the water power approximates 130,000 horse power; this probably represents a small proportion only of the total power available. This is of particular importance to the state, since it is relatively distant from coal supply. In 1905 the legislature appropriated $2,500 for a survey of the water powers and a report on them, and to this work the U. S. Geological Survey has contributed a like sum, in addition to having expended since 1902 a large amount for daily measurement of river flow. This bulletin presents in detail the information thus far accumulated, and the data given will be of great value to those immediately concerned.

4. *The Geological Survey of Cape of Good Hope; Twelfth Annual Report, 1907,* including the following papers: (1) Chairman's Letter, p. 3; (2) Director's Report, pp. 5–7; (3) Geological Survey of Parts of Vryburg, Kuruman, Hay and Gordonia, by A. W. Rogers, pp. 11-122, two maps and 13 figures; (4) Geological Survey of Portions of Mafeking and Vryburg, by A. L. DuToit, pp. 123–157, figs. 3; (5) Geological Survey of

Portions of Hopetown, Britstown, Prieska and Hay, by A. L. Du Toit, pp. 161–192, 1 fig. Cape Town, 1908.—Practically all of the work described in the reports mentioned has been done in territory heretofore unknown to geologists, and the Survey deserves much credit for its persistent study of inaccessible localities. It is surprising to find that the Cape Survey has been able to do such a large amount of creditable reconnaissance work, with a combined salary list of less than $5,000. H. E. G.

5. *Bergensfeltet og tilstödende Trakter i senglacial og postglacial tid;* af C. F. Kolderup. Bergens Museums Aarbog, 1907, No. 14, 8°, pp. 266, map and 38 figs.—The author has made a careful study of the ancient shore lines and surficial deposits in the region about Bergen on the west coast of Norway, and from these investigations draws certain conclusions regarding the movement of the ice during the last glacial period, the elevation and depression of the land with respect to the sea, and the effects of these upon the life of the period as shown by faunal groups.

The evidence shows a retreat of the ice, an interglacial period, and a renewed advance of the ice, and this is general and not confined to a single glacier. The faunal evidence is not conclusive that the interglacial time was essentially warmer. Since the different series of the terminal moraines in the Bergen district lie in the inmost parts of the fiords, the area must have been at that time comparatively free from ice, but that the glaciers attained the sea is shown by the fact that these moraines are stratified, and since they are 40–50 meters above the present sea-level the land was then correspondingly depressed. From this the land gradually sank to the level shown by the highest terraces which are found in all the large fiords, and which the writer designates as the Yoldia terraces. Then the ice retreated and the land rose to about its present position, not steadily but intermittently, with periods of rest which the author discusses. Morever, in postglacial time this was interrupted by an interval of downward movement, when the land stood some 10–14 meters lower than at present.

Divisions of time like those in the Christiania region cannot be carried out here since only the highest shell deposits, and not the corresponding clay beds with their contained fossils of postglacial time, have been elevated above the sea. Dredging, however, shows that they are present. Thus the available fossils are not decisive of conditions.

Finally shell deposits from Hardanger, Stord and Nordland are described.

The whole is an important addition to our knowledge of the glacial geology of western Norway. L. V. P.

6. *Mikroskopishe Physiographie der massigen Gesteine; Ergussgesteine* von H. Rosenbusch. 4te Auflage, 8°, pp. 717-1592. Stuttgart, 1908.—The appearance of the first part of the fourth edition of this great work has been already noted in this Journal (vol. xxiii, page 394, 1907). It is now completed in the

second part, which has recently been issued. This deals, as the title suggests, wholly with the effusive rocks, to which over half the work is thus dedicated. An advance over the last edition is to be noted in that age distinctions among these rocks is now done away with and, although the names are still given at each section heading, as basalt, diabase and melaphyre for example, the rocks and component minerals are treated collectively according to the plan followed in the author's Gesteinslehre. A new feature is the erection of the trachydolerite and of the lamprophyric lavas into independent rock groups.

This work is so well known and universally used that further comment is unnecessary. The new edition is a practical necessity for every working petrographer. The author is to be congratulated upon the completion of a task of such magnitude.

L. V. F.

7. *Die Fossilen Insekten und die Phylogenie der rezenten Formen;* von Anton Handlirsch. Pp. vii-ix, 1281-1430. Leipzig, 1908 (Wilhelm Engelmann).—This ninth part completes this very important work, which has been repeatedly noticed in these pages. An exhaustive index fills the closing twenty-seven pages.

8. *Gahnite from Charlemont, Mass.;* by George M. Flint (communicated).—A new locality for spinel has been added to the list of Massachusetts occurrences of this mineral, by the discovery, by the writer, of gahnite, at Charlemont, Franklin Co., in April, 1908. The mineral occurs in complex rocks, of highly metamorphic character, in the Hawley schist (hornblende-chlorite schist and hornblende-sericite schist) at a point near its contact with the Goshen schist. In this same series of rocks at a distance of about 4½ miles, air-line, the Rowe occurrence of this same mineral* is located. The material collected was taken from the dump of a newly developed pyrite mine about one-quarter of a mile south of the railroad station, and at the foot of the northeasterly slope of Mt. Peak.

The gahnite is in aggregates of black and greenish black crystals which commonly show a greenish color on fracture; also in the uncommon form of single crystals in quartz; and more rarely in a chloritic matrix, in which latter case it is associated with tremolite, chloritoid, feldspar, quartz, pyrite and some other minerals. The crystals range from 2 to 12^{cm} in length and many show the striated faces common in this species. The forms represented are the octahedron, octahedron modified by dodecahedron, and the octahedron twinned in accordance with the usual spinel law.

9. *Hints for Crystal Drawing;* by Margaret Reeks, with Preface by John W. Evans. Pp. xx, 148, with 44 plates. London, 1908 (Longmans, Green and Co.).—This small book gives detailed directions for the plotting of axes and the drawing of crystal figures upon them; a chapter on the drawing of twins is added. The directions are explicit and the study of the many

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* See A. G. Dana in this Journal, xxix, 455, 1885.

figures with which the book is illustrated should enable the student having some acquaintance with the methods of mechanical drawing to acquire considerable facility in the construction of such figures by following out the examples given. The methods, so frequently used to-day, of drawing crystal figures from the gnomonic or stereographic projections, are not discussed. W. E. F.

III. Botany.

1. *Systematic Anatomy of the Dicotyledons, A Handbook for Laboratories of pure and applied Botany;* by Dr. Hans Solereder, Professor of Botany in the University of Erlangen. Two volumes, Oxford, 1908. (The Clarendon Press.)—The translation has been carefully done by Messrs. L. A. Boodle and F. E. Fritsch, and revised by Dr. D. H. Scott. The text of the German edition is not easy to translate into smooth English, but the translators and editor, between them, have accomplished this in a remarkable manner. They have also cleared up some obscurities in the original, and have made the whole treatise entirely available to the English-speaking student.

Even before achromatic lenses began to reveal with certainty the forms of plant-tissues and their constituents, numerous investigators had carried on researches in this field and had begun to encumber the science of microscopic anatomy with useless terms. And, when the improved lenses unfolded surprises in every direction, the framework of plants was subjected by zealous students to a renewed and very thorough examination. The works which preceded the studies based on development were accurate and important, but they were excessively confusing, owing to a disregard of any convention as to terminology. The same term was often applied by different authors in different ways and different terms were not unfrequently applied to the same object. Again, there were some purists who insisted upon making the most absurd and minute distinctions and who revelled in complicated systems of tissues. For instance, it was not unusual to describe the innumerable variants in ordinary parenchyma, giving to each element a special name. After the scientific investigation of tissue development was fairly under way, certain new terms were introduced, but there was at the same time a disposition to clear away many of the old terms and much of the rubbish which had been so long accumulating. With the appearance of deBary's Comparative Anatomy a still further step was taken towards coördination, and from that time there has been a well-established consensus as to the use of technical terms.

From the foregoing can be gathered some idea of the enormous difficulty of the task undertaken by Solereder. It was nothing less than to sort out from the mass of heterogeneous material which had been so long in disordered heaps, the essential characters of tissues in all of our dicotyledonous plants. By an ingenious method of arrangement this was made not only clear but also useful. The well-ordered results are now accessible to histological students and to practical investigators of economic products, so that the treatise is useful, as the title-page says, for laboratories of pure and applied botany. The large treatise not only shows what has been done, but it also points out with mortifying sharpness the vast gaps in our knowledge of the histological morphology of plants.

Such a treatise is helpful by its stimulating character. It happens to be more than this. It indicates not only what has been done, and what there is to do, but it shows forcibly the worth of it all. In the concluding pages the author has given most valuable hints as to some speculative features of the subject, and although these are merely hints, they are likely to prove of profit to everyone who seriously studies the work. It is questionable whether the scientific world in general is aware of the deep obligation under which the English botanists are placing their fellow students by the publication of the recent important series of translations of German works in an attractive form. The present number of that series is one of the most valuable.

G. L. G.

2. *A Text-book of Botany and Pharmacognosy;* by HENRY KRAEMER, Ph.D. 3d Edition. Pp. viii, 850. Philadelphia, 1908 (Lippincott Co).—Prof. Kraemer's duties in connection with the Philadelphia College of Pharmacy have shown him the desirability of providing, for students of pharmacy and for pharmacists, a reference book which can answer the more important questions in regard to the structure of medicinal plants and the principal characters of their useful products. The morphology of plants in general and the special morphology of the higher plants are treated in part first in considerable detail, and this is followed by comprehensive studies of the different families of plants yielding drugs. The sequence of families is that generally adopted, namely proceeding from the lower to the higher, closing with Compositæ. It is well known to our readers that now-a-days, the practical study of Botany is no longer insisted upon as an introduction to medical training, largely because the preparation of medicinal agents from the vegetable kingdom has fallen properly into the hands of specialists known as pharmacists. It was plausibly asserted that medical students did not have time which could be given to a subject like Botany, so remote from their daily needs as practitioners, and although regrets were expressed that a study so well fitted for preparatory discipline must be given up, it disappeared quietly from the list of obligatory subjects. Even in those European universities which still retain it in the medical curriculum, its tenure is most precarious. However, practical Botany is safe in the charge of the excellent pharmacists now conducting our best schools of pharmacy. From the first part of Professor Kraemer's book, the student can

obtain the facts which he needs in regard to the forms and affinities of the higher plants, but will find in the treatise hardly anything which may be called vegetable physiology, a subject which examines the way in which medicinal as well as other plants create their useful products. Some valuable hints in regard to plant life are given here and there, but it is to be hoped that in a fourth edition of the text-book, the chapter on the cultivation of medicinal plants may be so enlarged as to comprise the underlying principles of plant-functions. The second part of the book is given up to the examination of drugs, and is well proportioned. More liberal use could well have been made of photomicrography, for the original illustrations as well as the copies are most helpful. Professor Kraemer will perhaps hereafter give greater definiteness to some of the statements regarding very interesting points, which would be excellent subjects for work by his advanced students; such, for instance, as Hamamelis. Excellent tables and keys make the work handy in the best sense of the term, and render it useful for food- and drug-analysts as well as pharmacists. In important particulars it supplements some recent trustworthy treatises which are chiefly devoted to food-products. For American students who are not familiar with French or German, the present volume of Pharmacognosy will prove invaluable. G. L. G.

3. *Die Gestalts- und Lageveränderung der Pflanzen-Chromatophoren;* mit einer Beilage: Die Lichtbrechung der lebenden Pflanzenzelle; von Gustav Senn. Pp. xv, 397, with 83 text-figures and 9 plates. Leipzig, 1908 (Wilhelm Engelmann).—In this volume the author has given the most complete account of the changes in form and position of chlorophyll-grains and color-granules which has yet been published. Its value is much enhanced by the excellent table of contents and an exhaustive index, but it is even more increased by what is, until recently, lacking in most German treatises upon similar subjects, namely, clear and comprehensive summaries or abstracts, at convenient points throughout the work. When we remember that the differentiated protoplasmic bodies which are collectively termed Plastids, play such an important part in all plant activities, everything which can add to the knowledge of the behavior of these under external and internal influences must be heartily welcomed. Dr. Senn has given us a well-proportioned treatise which embodies the most essential features of the literature of the subject, and has also added a supplement which considers a cognate matter of great importance, namely, the refractive power of living vegetable cells. He gives to the clear cell-wall and its lining of protoplasma the refractive index 1·47 to 1·52, while that of the cell-sap therein contained is only a trifle higher than that of water. From these figures it is not difficult to determine the distribution of light and shade within the cells of living plants. The bearing of this on the subject of ecology is very plain. G. L. G.

IV. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *National Academy of Sciences.*—The autumn meeting of the National Academy was held in Baltimore on November 17–18. About thirty-five members were in attendance. The following is a list of the titles of papers presented:

H. F. OSBORN : The close of the Cretaceous and beginning of the Eocene in the Hell Creek region of Montana ; based on explorations of the American Museum between 1902 and 1908.
A. G. WEBSTER : On the distribution of sound from the megaphone, or speaking trumpet.
H. S. JENNINGS : Elementary species and the effects of selection in a unicellular organism.
R. W. WOOD : Absorption spectra of mixtures of metallic vapors. The mercury paraboloid as a reflecting telescope.
H. N. MORSE : Results obtained in the direct measurement of osmotic pressure.
SIMON FLEXNER : Certain examples of bio-chemical control of cell development. (*a*) Metaplasia of transplantable tumors ; (*b*) Inhibition of Spirocheta pallida.
R. H. CHITTENDEN : Further studies on the effect of a low protein diet on high protein animals.
ALEXANDER AGASSIZ : The work of the U. S. Fish Commission ship "Albatross."
A. AGASSIZ and H. L. CLARK : The Echini of an insular fauna.
H. C. JONES and J. A. ANDERSON : The absorption spectra of solutions of certain salts.
JOHN B. WATSON : The reactions of primates to monochromatic lights.
E. G. CONKLIN : Effects of centrifugal force on the organization and development of the eggs of certain animals.
C. R. VAN HISE : The phosphates of the soil.
B. O. PEIRCE : Biographical memoir of Joseph Lovering.
W. H. DALL and W. H. BREWER : Biographical memoir of William M. Gabb.
CHARLES S. HASTINGS : Biographical memoir of Josiah W. Gibbs.

2. *National Antarctic Expedition, 1901–1904. Meteorology. Part I.* Observations at Winter Quarters and on Sledge Journeys, with discussions by various authors. Pp. xiv, 548, with 4 maps, London, 1908. (Published by the Royal Society.)—It will be remembered that the explorations of the National Antarctic Expedition, between 1901 and 1904, were carried on by the ship "Discovery" under command of Commander R. F. Scott. The ship wintered at the south extremity of Ross Island in latitude 77° 51′, and longitude 166° 45′ E., in close proximity to the lofty volcanoes of Mt. Erebus and Mt. Terror.

The present volume gives the results of the meteorological observations of the expedition made under the direction of Lieut. Royds. The complete record of observations taken at the winter quarters is given in detail and also that of the sledge journeys, of which the journey of Captain Scott reached 82° 16′ 33″ south latitude. The range of temperature observed was from a maximum of 42° F. to a minimum of —58·5°, with very rapid and violent fluctuations at all seasons but not always associated with changes of wind direction. It was found that polar winds brought with them an increase of temperature. The summers were remarkably cold with but few days having a mean temperature above 32°. The highest daily mean noted was 26 2° and the lowest —21°. The air was found remarkably dry and transparent with but little fog and slight precipitation, and the sunshine was remarkably abundant. In December, 1903, for example, an average of 16 hours per day was registered. The range of pressure was between 30·181 and 28·140 inches, and the observations showed the common semi-diurnal oscillations amounting to ·002 inches. Other interesting points are brought out in the report, which gives also a summary of results at other stations in the antarctic. The volume is accompanied by a series of large maps and some excellent reproductions of views and of solar phenomena.

Physical Observations with discussions by various authors. Pp. v, 192, 21 plates, 2 maps.—The subjects discussed in this volume are as follows: Tidal observations in the Antarctic, 1902–3; pendulum observations; earthquakes and other earth movements recorded in the Antarctic, 1902–3; auroral observations 1902–3; magnetic observations, 1902–4. The magnetic observations have a particular interest because they were carried on at numerous points in the proximity of the south magnetic pole. The probable position of the pole was determined independently by observations of the declination, and also by those of the inclination. The results obtained in the two cases agree within a few minutes of each other. The mean of the two positions, viz. latitude 72° 51′ S., longitude 156° 25′ E., is regarded as a close indication of the center of the polar area. This position places the pole about 200 geographical miles east of the place assigned to it by Sabine (1841), indicating a probable change of position in this direction.

It is noted that the auroral displays, although frequent, were in general extremely poor. A series of excellent plates, however, represent some exceptional cases of striking character; in these irregular bands, made up of rays or vertical shafts close together, formed the so-called draped auroræ.

3. *Road Preservation and Dust Prevention;* by WILLIAM PIERSON JUDSON. Pp. 146. New York, 1908 (The Engineering News Publishing Co.).—The subject of this book is one in which recent developments have made our communities more deeply interested than ever before, viz., the preservation of the surface of macadamized roads and the prevention of dust in connection with them. Those concerned with this topic will find the matter presented from the practical standpoint, with a careful consideration of the various methods that have been suggested for accomplishing the ends in view.

4. *Ostwald's Klassiker der Exakten Wissenschaften.* Leipzig, 1908 (Wilhelm Engelmann).—The following list includes the titles of recent additions to this valuable series of scientific classics (cf. xxv, p. 534).

Nr. 163. Chemisch-optische Untersuchungen; von J. H. JELLETT. Übersetzet von L. FRANK. Herausgegeben von W. NERNST. Pp. 84, mit 6 Figuren im Text.

Nr. 164. Newton's Abhandlung über die Quadratur der Kurven (1704). Aus dem Lateinischen übersetzt und herausgegeben; von GERHARD KOWALEWSKI. Pp. 66, mit 8 Textfiguren.

Nr. 165. Neue Stereometrie der Fässer, besonders der in der Form am meisten geeigneten österreichischen, und Gebrauch der kubischen Visierrute. Mit einer Ergänzung zur Stereometrie des Archimedes; von JOHANNES KEPLER. Linz 1615, Druck von JOHANNES PLANK. Aus dem Lateinischen übersetzt und herausgegeben von R. KLUG. Pp. 130, mit 29 Figuren im Text.

5. *Elementary Dynamics;* by ERVIN S. FERRY, Professor of Physics in Purdue University. Pp. 182. New York, 1908 (The Macmillan Company).—A teacher interested in his work is apt to feel like giving it permanent form in a text-book. But in most cases his methods are so peculiar to himself as to render the book of little value out of his own hands, and this is the chief reason why half the elementary text-books have so little excuse for going before the public. This is especially true of text-books on Mechanics, for in them preëminently peculiarities are apt to be faults—and their besetting fault is bad logic.

These criticisms do not apply to Professor Ferry's book, for reasons which best appear from the author's statement in the preface of his conception of how this difficult subject should be presented to beginners:

"All technical terms should be accurately and succinctly defined. In all definitions the physical nature of the thing has been emphasized instead of the mathematical formula which expresses its magnitude. * * The number of propositions derived from experience and experiment that are to be taken as fundamental should be as few as possible. It has been found that, with the exception of the properties of matter, all the laws of dynamics can be deduced from five simple propositions derived from experience and experiment. * * The laws of the subject should be deduced from the definitions and fundamental principles by rigid methods whenever the advancement of the student will justify it. To habitually accept without proof such laws as the parallelogram of forces because they agree with experience induces a flabby condition of the mind. It is, however, more dangerous to employ mathematical methods with which the student has had insufficient practice." W. B.

6. *Plane and Solid Geometry;* by ELMER A. LYMAN. Pp. 340. New York, 1908 (American Book Company).—This is a book through which the student must work his way, relying on his reasoning powers rather than on his memory. The subject

matter is very much abridged, many unimportant theorems being inserted as exercises. The treatment of the Theory of Limits is very much simplified. Historical notes are introduced extensively and add much to the value of the book.

7. *Moral Instruction and Training in Schools. Report of an International Inquiry.* Two volumes, edited by M. E. SADLER. Vol. I, The United Kingdom; pp. lv, 538. Vol. II, Foreign and Colonial; pp. xxvii, 378.—The investigations which have yielded the results given in these volumes had their origin in a private conference held in London in the autumn of 1906, to consider what steps could be taken to improve the moral instruction and training in schools. A provisional committee was appointed at that time and, later, the council was joined by several hundred persons, an executive committee being appointed on February 5, 1907. A committee for the United States was also selected with Dr. Nicholas Murray Butler as chairman.

Volume I contains, after the introduction by Prof. M. E. Sadler, a series of 33 chapters by different authors, discussing the subject from different standpoints in its relation to schools in Great Britain and Ireland. The second volume continues the discussion in a series of 24 chapters, as related to the schools of France, Germany, Switzerland, Belgium, Norway, Denmark, the United States, Canada, Australia, New Zealand and Japan. A large and varied amount of information is thus presented to the interested public.

8. *Practical Exercises in Physical Geography;* by WILLIAM MORRIS DAVIS. Pp. 144, with atlas containing 45 pls. (45 pp.) New York, 1908 (Ginn & Company).—The study of land forms, as a part of the instruction in physical geography in high schools, has not commended itself to a great many successful teachers. The trouble has been that illustrations of different stages of the development of land forms were not at hand. "Practical Exercises" will do much to remedy this defect. The method of illustration by block diagrams, as used in the "atlas," will readily commend itself to all students of physical geography. H. E. G.

9. *Twenty-Sixth Annual Report of the Bureau of American Ethnology.* 1904–5. Pp. xxxi, 512, LVIII plates, 117 figures. Washington, 1908 (Government Printing Office).—The present volume contains the adminstrative report of the Chief of the Bureau, W. H. Holmes; also two extended memoirs, one by Frank Russell on the Pima Indians (pp. 3–389), and the second by John R. Swanton on the Social Condition, Beliefs and Linguistic Relationship of the Tlingit Indians of Alaska (pp. 391–485). Both papers are liberally illustrated with excellent plates, in addition to text-figures.

OBITUARY.

Dr. WILLIAM K. BROOKS, Professor of Zoology in Johns Hopkins University, and author of numerous important contributions on zoological subjects, died in Baltimore on November 12 in his sixty-first year.

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[*] This Index contains the general heads. BOTANY, CHEMISTRY (incl. chem. physics), GEOLOGY, MINERALS, OBITUARY, ROCKS, ZOÖLOGY, and under each the titles of Articles referring thereto are mentioned.

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