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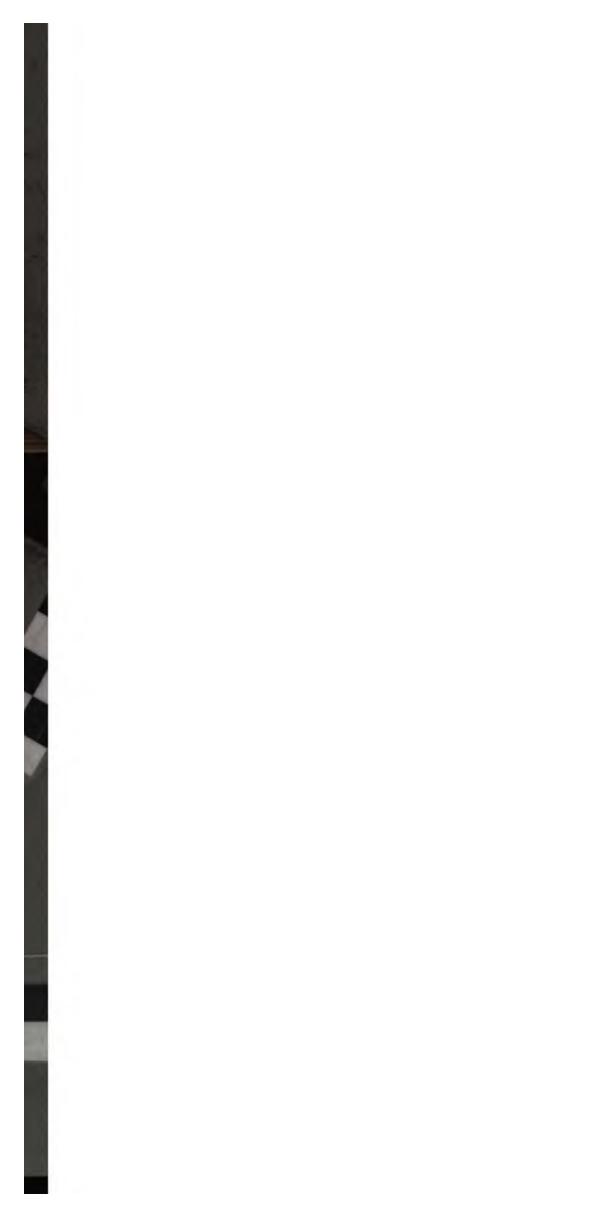
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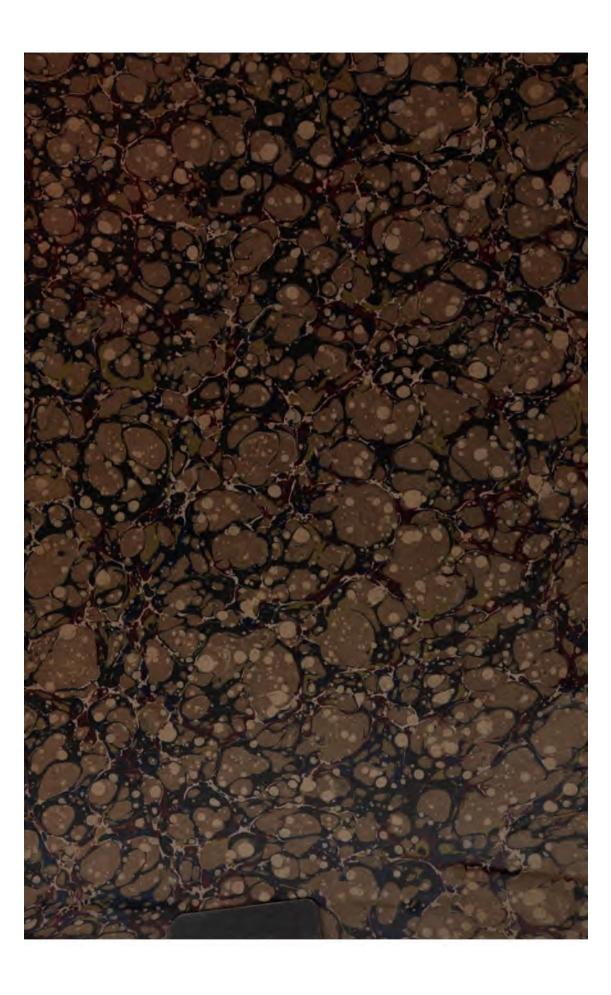
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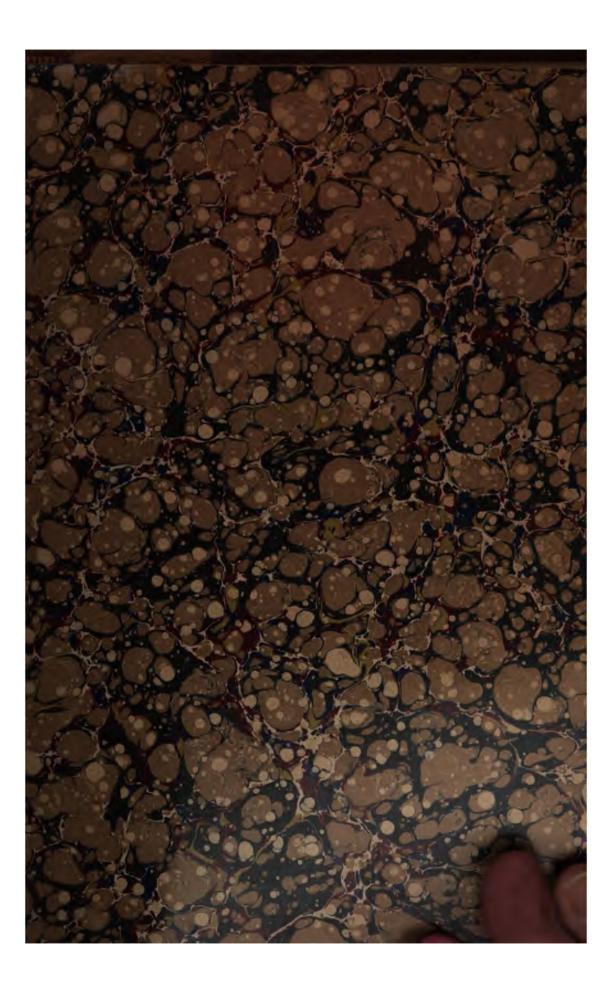
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# CONTRIBUTIONS TO COSMOGONY AND THE FUNDAMENTAL PROBLEMS OF GEOLOGY

# THE GASES IN ROCKS

BY

# **BOLLIN THOMAS CHAMBERLIN**

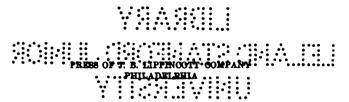


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# THE GASES IN ROCKS.

It has been known for a long time from microscopical studies that some minerals inclose minute cavities which contain both liquid and gaseous matter. For a much shorter period it has been known that various igneous rocks, when exposed to red heat in a vacuum, evolve several times their volume of gas of quite variable composition. Since these gases occur in proportions entirely different from those of the constituents of the air, it has not seemed probable that they were derived directly from our present atmosphere, unless the rocks manifest some power of selective absorption not now understood. The apparent difficulties involved in this conception have suggested that some earlier atmosphere was rich in those gases. This involves a hypothesis relative to the changes through which the atmosphere has passed, and leads on to a theory of its origin and that of the earth itself. An alternative hypothesis regards these gases, not as the products absorbed by a molten earth from its surrounding gaseous envelope, but as entrapped in the body of the earth during its supposed accretion, and hence that they are a source from which accessions to our present atmosphere might be derived.

A study of these gases in the rocks has seemed, therefore, to give promise of results of some value to atmospheric problems and, perhaps, to those of cosmogony. Because of this, it appeared advisable to determine more widely the range and the distribution of these gases, their relations to other geologic phenomena, and the states in which the gases, or gasproducing substances, exist in the rocks. The desirability of supplementary work will become more evident when it is noted that, while a considerable number of investigators have analyzed the gases in rocks, as will appear in the following historical statement, nearly all have contented themselves with a few determinations, and that even a full compilation of all such results leaves much to be desired from a geological point of view.

### HISTORICAL SKETCH.

As early as 1818 the attention of Sir David Brewster was called to the subject of inclosed water by the explosion of a crystal of topaz when heated to redness; but his studies were not published until 1826. In the mean time, Sir Humphry Davy opened the cavities in a few crystals and examined chemically the imprisoned liquid and gas.<sup>1</sup> Piercing a cavity in several cases suddenly caused the inclosed gas-bubble to contract to from one-sixth to one-tenth of its original volume. The gas was thought to be pure nitrogen. The basaltic rock from the neighborhood of Vicence con-

<sup>&</sup>lt;sup>1</sup>Sir Humphry Davy, Phil. Trans. 1822, Pt. 11, pp. 367-376; Ann. de Chim. et Phys., t. 21 (1822), pp. 132-143.

tained gas (supposedly nitrogen) in a still more rarefied state, as its density was 60 to 70 times less than that of the atmospheric air. Upon perforating a cavity in a quartz crystal from Dauphiné, an almost perfect vacuum was discovered. Davy regarded the rarefied condition of the inclusions in the crystals as strong evidence that the waters and gases did not penetrate the crystals at ordinary temperatures and pressures. This he believed a decisive argument in favor of the Huttonian, or Plutonian, school. However, a crystal from Brazil gave a very different result; an immediate expansion to a volume 10 to 12 times greater than the original followed the opening of a cavity. The composition of the gas was not determined. The existence of compressed gas in the same sort of cavities seems adverse to the conclusions which Davy based upon his earlier experiments, but he sought to explain the difference by supposing the crust to have been formed under a pressure more than sufficient to balance the expansion due to the heat.

Brewster attacked the problem by observing the temperature at which the inclosed liquid passed over into the gaseous state. A number of tests showed this to range from 74° to 84° F. When raised to this temperature the vacuity always reappeared. Brewster interpreted as follows:

The existence of a fluid which entirely fills the cavities of crystals at a temperature varying from 74° to 84° may be held as a proof that these crystals were formed at the ordinary temperature of the atmosphere.

For thirty years after Brewster the field was neglected until, in 1858, Simmler<sup>2</sup> reviewed Brewster's work in the light of advancing scientific knowledge. Studying the liquid inclusions in quartz, topaz, amethyst, garnet, and other minerals, he arrived at the conclusion that the power of expansion of the liquid in these inclusions showed it to be carbon dioxide. Some years later Sorby, continuing the researches along the lines suggested by Brewster and Simmler, found that the amount of expansion of liquid carbon dioxide from 0° C. to 30° C. corresponded closely to that observed in the liquid of the sapphires with which he experimented.\* In these sapphires it was noted that the liquid disappeared when warmed to approximately 30° C. As the critical temperature for carbon dioxide, above which no amount of pressure will condense it to a liquid, is 30.92° C. (87.7° F.), there remained little room for doubt that the gas was largely carbon dioxide. Sorby remarked that this gas "might have been inclosed, either as a highly dilated liquid or as a highly compressed gas; but since the other liquid has deposited crystals which dissolve on the application of heat, it seems most probable that the water was caught up in a liquid state, sometimes, perhaps, holding a considerable amount of carbon dioxide in solution as a gas."

In the same year Vogelsang and Geissler heated quartz crystals and, passing an electric spark through the gas thus liberated, examined its

Sir David Brewster, Trans. Roy. Soc. Edinburgh, vol. 10 (1826), pp. 1-41; Edin. Jour. of Science, vol. 6, pp. 153-156.
 R. T. Simmler, Pogg. Ann., vol. 105 (1858), pp. 460-466.
 H. C. Sorby and P. J. Butler, Proc. Roy. Soc., vol. 17 (1869), pp. 291-303. Earlier papers by Sorby appeared as follows: Phil. Mag., 4th series, vol. 15, p. 152; Quart. Jour. Geol. Soc., vol. 14 (1858), p. 453; Proc. Roy. Soc., vol. 13 (1864), p. 333.
 Saline water.
 Vogelsang and Geissler, Pogg. Ann., vol. 137 (1869), pp. 56-75.

spectrum, which was found to show the presence of much carbon dioxide, together with water and a very weak trace of hydrogen. The presence of the hydrogen line, however, the authors were inclined to attribute to water-vapor.

Further researches upon the critical point of the gas in mineral cavities, carried on by Hartley, yielded results varying from 26° to 34° C. The lowering of the temperature he ascribed to the presence of some incondensable gas, perhaps nitrogen, while he believed that the raising of the critical point observed in some of the quartz specimens was due to hydrochloric acid.

Forster<sup>2</sup> and Hawes<sup>3</sup> investigated smoky quartz, the former distilling from the Tiefengletscher crystals a brown fluid of an empyreumatic odor, giving reactions for ammonia and carbonic acid, from which he concluded that the coloring matter of smoky quartz was due to a nitrogenous hydrocarbon, decomposable by heat; the latter made a microscopic study of the liquid carbon dioxide in the bubbles of the cavities.

Investigations which have opened up a broader field were begun by Graham' in 1867 upon the Lenarto meteoric iron. By submitting a strip of the iron to a red heat in a vacuum for 35 minutes he obtained 5.38 cubic centimeters of gas from 5.78 cubic centimeters of the metal. Heated for an additional 100 minutes, there were evolved 9.52 cubic centimeters of gas having the following composition: H<sub>2</sub>, 85.68; CO, 4.46; CO<sub>2</sub>, none; N<sub>2</sub>, 9.86.

As this meteorite yielded about three times its volume of gas, and since "it has been found difficult, on trial, to impregnate malleable iron with more than an equal volume of hydrogen, under the pressure of our atmosphere," Graham drew the inference that this meteorite came from a body having a dense atmosphere of hydrogen gas. By the same process Mallet sextracted 3.17 volumes of gas from a Virginia meteorite. His results were in accordance with those of Graham: H2, 35.83; CO, 38.33; CO<sub>2</sub>, 9.75; N<sub>2</sub>, 16.09.

Wöhler heated to redness some of the metallic granules from the iron basalt of Ovifak, Greenland, obtaining more than 100 volumes of gas which burned with a bluish flame (mostly carbon monoxide mixed with a little of the dioxide). His results, however, were vitiated by having used an iron combustion tube.

Pursuing the method adopted by Graham and Mallet, A. W. Wright<sup>7</sup> conducted a series of experiments on meteorites, which have remained to the present day the source of most of our knowledge of the gas content of these interesting bodies. Wright's chief contribution lies in his two tables showing that there is a marked difference between the gas contents of the iron and stony types of meteorites; for while, in the former, hydrogen is

W. N. Hartley, Jour. Chem. Soc. (1876), vol. 2, pp. 237-250.
 A. Forster, Pogg. Ann., 143 (1871), pp. 173-194.
 G. W. Hawes, Am. Jour. Science, vol. 21 (1881), pp. 203-209.
 Thos. Graham, Proc. Roy. Soc., vol. 15 (1867), p. 502.
 J. W. Mallet, Proc. Roy. Soc., vol. 20 (1872), pp. 365-370.
 F. Wöhler, Pogg. Ann., 146 (1872), pp. 297-302.
 A. W. Wright, Am. Jour. Science, vol. 9 (1875), pp. 294-302 and 459-460; vol. 11 (1876), pp. 253-262; vol. 12 (1876), pp. 165-176.

the most abundant gas, carbon dioxide is the most characteristic constituent of the latter. His analyses are given in table 1.

TABLE 1.

Meteorite.	CO <sub>2</sub> .	co.	CH4.	H <sub>2</sub> .	N <sub>2</sub> .	Vol.
Iron meteorites: Tazewell County, Tenn	14.40	41.23		42.66	1.71	3.17
Shingle Springs, Cal Arva, Hungary	13.64	12.47 67.71		68.81 18.19	5.08 1.54	0.97 47.13
Texas	8.59 13.30	14.62 15.30		76.79 71.40		1.29
Stony meteorites:		4.40	2.05	31.89	1.78	2.99
Guernsey, Ohio	60.29	4.35 1.74	3.61 2.08	29.50 13.59	2.25 1.57	1.75 2.63
Parnallee, India	80.78	2.20 1.80	1.63 0.0	13.06 57.88	2.33 4.88	3.49 2.50

This table shows that in the iron meteorites carbon dioxide in no case constituted more than 15 per cent of the gas evolved, while in every case but one the quantity of carbon monoxide was considerably greater. In the stony meteorites carbon monoxide is low, while carbon dioxide is, in the majority of analyses, much the most abundant gas. Hydrogen is more important in the iron meteorites than in the stony.

The same experimenter determined also the gases given off by the same meteorite at different temperatures. His figures for the Iowa County meteorite are shown in table 2.

TABLE 2.

Gas.	At 100°.	At 250°.	Below red heat.	At low red heat.	At full red heat.
Carbon dioxide	.00 4.54	92.32 1.82 5.86 0.00	42.27 5.11 48.06 4.56	35.82 0.49 58.51 5.18	5.56 0.00 87.53 6.91
Total	100.00	100.00	100.00	100.00	100.00

The progressive decrease in the percentage of carbon dioxide and the corresponding increase of hydrogen with the elevation of the temperature are striking. His inquiries into other phases of the problem will be deferred until the discussion of principles, where it will be possible to treat each factor to better advantage, in its proper relation to the whole subject.

Several years later Wright applied his method of gas extraction and reliable quantitative analysis to the gases in smoky quartz, which heretofore had been subjected chiefly to qualitative microscopical studies. However, only one determination was made—that of a crystal from Branchville, Connecticut, which yielded a small quantity of gas of the following composition: Carbon dioxide, 98.33; nitrogen, 1.67; hydrogen sulphide, sulphur dioxide, ammonia, fluorine, and chlorine, trace.

<sup>&</sup>lt;sup>1</sup>Wright, Am. Jour. Science, vol. 21 (1881), pp. 209-216.

Wright regarded the fluorine and chlorine as being combined, and the ammonia as probably existing together with some of the carbon dioxide in the form of ammonium carbonate. The amount of water obtained, calculated as vapor, was slightly more than twice the volume of carbon dioxide.

Following Wright, Sir James Dewar, in collaboration with Mr. Ansdell, made several more analyses of the meteoritic gases, and then, in an endeavor to discover the source and significance of these gases, directed a series of experiments upon the theory that graphite might be the retentive or generative constituent. Their analyses of the gases from graphites and from the matrix from which graphites have come revealed moderately high volumes.

Table 3.

Material.	Sp. gr.	Vol.	CO2.	co.	Hg.	CH <sub>4</sub> .	N <sub>2</sub> .
Celestial graphite	2.86 2.05 2.25	7.25 2.60 2.55 0.22 7.26 5.32 1.27	91.81 36.40 57.41 66.60 50.79 82.38 94.72	7.77 6.16 14.80 3.16 2.38 0.81	2.50 22.2 10.25 7.40 2.50 13.61 2.21	5.40 26.11 20.83 3.70 39.53 0.47 0.61	0.1 6.66 4.16 4.50 3.49 1.20 1.40

Because the quantity of gas yielded by these specimens of graphite was so considerable, Dewar proceeded to ascertain whether graphite could absorb the different gases when allowed to stand in each of them for 12 hours. His experiments with the celestial graphite which had previously been deprived of its gases indicated that little or no absorption had taken place. "It is therefore evident," says Dewar, "that the large quantities of gas occluded in celestial meteorites can not be explained by any special absorptive power of this variety of carbon." Attempts to split up the hydrogen-producing compound with strong nitric acid and also to wash out, with ether, the possible carbonaceous source of the methane, appeared to show that the hydrogen existed in a very stable compound, and that, while the ether lessened the quantity of methane which the graphite afterwards furnished, it did not dissolve out all the carbonaceous compounds present, or else that the marsh-gas was subsequently formed during the heating of the material.

Dewar's analyses of gases from stony meteorites, which are in accord with Wright's results, are given in table 4.

TABLE 4.

Meteorite.	8p. gr.	Vol.	CO <sub>2</sub> .	CO.	H <sub>2</sub> .	CH <sub>4</sub> .	N <sub>2</sub> .
Dhurmsala, India Pultusk	3.718 3.67	2.51 3.54 1.94 0.55	63.15 66.12 64.50 39.50	1.31 5.40 3.90 18.50	28.48 18.14 22.94 25.4	3.9 7.65 4.41	1.31 2.69 3.67 16.60

An analysis of the gas extracted from the Orgueil meteorite revealed much sulphur dioxide, which Professor Dewar believed to have been derived

<sup>&</sup>lt;sup>1</sup> Dewar and Ansdell, Proc. Roy. Inst., vol. 11 (1884–1886), p. 332 and pp. 541–552.

from the decomposition of sulphate of iron. In all, 57.87 volumes were obtained: CO<sub>2</sub>, 12.77; CO, 1.96; CH<sub>4</sub>, 1.50; N<sub>2</sub>, 0.56; SO<sub>2</sub>, 83. Leaving out the SO<sub>2</sub>, 9.8 volumes remain, as follows: CO<sub>2</sub>, 76.05; CO, 11.67; CH<sub>4</sub>, 8.93; N<sub>2</sub>, 3.33. This analysis, the most remarkable of the series, though Dewar does not mention the fact, shows a complete absence of hydrogen (an uncommon phenomenon), while the percentage of marsh-gas is unusu-There is, however, reason to suspect that there was hydrogen liberated, but that it was oxidized to water by the action of the iron compound, following the decomposition of the sulphate.

In 1888 W. F. Hillebrand discovered that the mineral uraninite when treated with acids slowly disengaged bubbles of gas. As the result of a well-selected series of tests this appeared, in the light of the chemical knowledge of that day, to be nitrogen. Trials with different varieties of the mineral revealed a rather significant relation between the percentage of uranyl and this gas. The greater the amount of the oxide, the more gas obtained.

Several years later, Sir William Ramsay's scepticism was aroused when his attention was called to the paper by Hillebrand, for he hesitated to believe that free nitrogen could be produced by treating any substance with sulphuric acid. To test the case, he decomposed cleveite with this acid, obtaining little nitrogen, but some 20 cubic centimeters of argon, which the spectroscope showed to be mixed with some other gas.<sup>2</sup> A brilliant yellow line which appeared in this spectrum coincided exactly with D<sub>3</sub>, the so-called "helium" line, first discovered in the spectrum of the chromosphere of the sun by Sir Norman Lockyer in 1868. This was the first real acquaintance with helium, until then known only as a hypothetical substance existing in the sun. Lockyer immediately became interested in this discovery of helium in a terrestrial mineral, and attempted to prove that it was not a single gas, but a compound or a mixture of gases, basing his contention upon various strange lines in the spectrum.

Ramsay, continuing his study of the gas from cleveite, perceived what had been previously overlooked, namely, that hydrogen generally was more abundant than helium—in one case amounting to 80 per cent of the total The hypothesis that this hydrogen might have been formed by the breaking up of an unstable hydride, the form in which Ramsay thought the helium should be evolved, if it were derived from combination with the uranium or yttrium of the mineral, was put to the test, with the result that the evidence pointed strongly against the theory.4 A series of minerals powdered and fused with potassium acid sulphate were found to yield gas, sometimes helium, but oftener hydrogen and the oxides of carbon.

In 1896 W. A. Tilden made an attempt to determine the condition in which helium and the associated gases exist in minerals. Argon and helium were of particular interest, for Tilden believed that these two elements will

W. F. Hillebrand, Bull. 78, U. S. G. S., pp. 43-79.
 Sir William Ramsay, Proc. Roy. Soc., vol. 58 (1895), pp. 65-67.
 Sir J. N. Lockyer, a series of six short papers in Proc. Roy. Soc., vols. 58, 59, and 60.
 Ramsay, Proc. Roy. Soc., vol. 58, pp. 81-89.
 Ramsay, Proc. Roy. Soc., vol. 59, pp. 325-330.
 Ramsay and Travers, Proc. Roy. Soc., vol. 60, pp. 442-448.

not be found to enter into combination at such temperatures as are ordinarily attainable. In his own words:

It also appears improbable that in the minerals from which the mixture of gases containing helium has been extracted this element exists in a state of ordinary chemical combination, for, on treating the mineral with acids, no compound of helium with hydrogen has yet been observed, and the components of the minerals are of a kind which are commonly regarded as chemically saturated.1

The minerals monazite and cleveite were found to yield gas at low temperatures (60° and 110°, respectively), carbon dioxide appearing first. monazite heated to 130° to 140° gave gas which, for the first time, showed the D<sub>3</sub> line, indicating the presence of helium. Between 140° and 250° there was obtained carbon dioxide with about one-fourth of its volume of a gas rich in helium. At higher temperatures up to 446° (boiling sulphur) there was less gas evolved. Cleveite behaved in a similar way. Studies on the absorption of helium by cleveite demonstrated that the mineral does not absorb this gas at the ordinary pressure, although placed in a helium atmosphere for nine weeks. But under pressure of 2.5 and 7 atmospheres, Tilden believed that he obtained an appreciable absorption. A trial with the Peterhead granite, which contained no helium in the first place, proved that the granite would absorb none of the gas whatever, even aided by a pressure of 7 atmospheres.

The finding of hydrogen as well as carbon dioxide in this Peterhead granite<sup>2</sup> led Tilden to investigate the gases inclosed in crystalline rocks.<sup>3</sup> His five complete analyses are as given in table 5.

TABLE 5.

Rock.	CO <sub>2</sub> .	co.	СН4.	H <sub>2</sub> .	Ng.
Granite, Skye. Gabbro, Lizard Pyroxene gneiss, Ceylon Gneiss, Seringapatam Basalt, Antrim	5.50 77.72 31.62	5.36	3.02 2.03 0.56 0.51 10.00	61.68 88.42 12.49 61.93 36.15	5.13 1.90 1.16 0.56 1.61

In addition to these analyses, 25 carbon-dioxide determinations were

Tilden believed the gas to be "wholly inclosed in cavities which are visible in thin sections of the rock when viewed under the microscope. \* To account for the large proportion of hydrogen and carbon dioxide in these gases, it is only necessary to suppose that the rock inclosing them was crystallized in an atmosphere rich in carbon dioxide and steam, which had been, or were at the same time, in contact with some easily oxidizable substance, at a moderately high temperature. Of the substances capable of so acting, carbon, a metal, or a protoxide of a metal present themselves as the most probable." Hydrogen and carbon monox-

W. A. Tilden, Proc. Roy. Soc., vol. 59 (1896), p. 218.
 Wright's two analyses, showing that trap rocks yield much the same gases as meteorites, also served to call attention to this field for investigation.
 Tilden, Chem. News, vol. 75 (1897), pp. 169-170.

ide might then be produced by the reducing action of metallic iron or ferrous oxide upon steam and carbon dioxide at high temperature, according to the reactions—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$
  $3Fe + 4CO_2 = Fe_3O_4 + 4CO$ 

The origin of the marsh-gas is assigned in this paper to the action of water at high temperature upon metallic carbides, or similar compounds, in the earth's interior, as suggested by Mendeléef and the more recent studies of Moissan.2

A year after the publication of Tilden's article, criticism of his paper, and in fact of the work of all previous investigators in this line, was made by M. W. Travers, who undertook to prove that the different gases, not excluding even argon and helium, did not exist in the gaseous state in minerals, but were formed by chemical interaction between the non-gaseous materials in the combustion-tube.\* The key to his position lay in the two reversible reactions-

$$3\text{FeO} + \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + \text{H}_2$$
  $3\text{FeO} + \text{CO}_2 = \text{Fe}_3\text{O}_4 + \text{CO}$ 

His table revealed a certain relation between the hydrogen and carbon monoxide produced, and the quantity of ferrous oxide and water present in the mineral. It is shown in table 6. The figures for FeO and H<sub>2</sub>O refer to the percentages in the rock; the gases are expressed in cubic centimeters per gram of rock.

TABLE 6.

Mineral.	FeO.	H₂O.	H <sub>2</sub> .	co.	CO <sub>2</sub> .
Chlorite, Moravia Serpentine, Zermatt. Gabbro, Isle of Skye Mica, Westchester, Pa. Foliated talc, Tyrol Feldspar, Peterhead.	2.7 6.1 1.4 0.4	9.5			

Four of these (including the mica of meta-sedimentary origin) were secondary minerals whose gas may have been produced entirely by chemical reactions in the tube, without having very great bearing upon the problem of the gas-content of primary minerals and rocks which have not undergone extensive weathering and alteration. The only rock tried, the gabbro, may be pointed out as unique in yielding only hydrogen without either of the oxides of carbon or nitrogen.

Armand Gautier,4 in 1901, came to the conclusion that the gases which he obtained from several igneous rocks did not escape from inclusions, for the most part, but were products of chemical reactions at raised temperatures. A small quantity of gas was obtained by heating granite powder, moistened with pure water, up to 300° in a vacuum. By heating the same

Mendeléef, Prin. of Chem., transl. of Kamensky and Greenaway, vol. 1, pp. 364–365.
 H. Moissan, Proc. Roy. Soc., vol. 60 (1896), pp. 156–160.
 M. W. Travers, Proc. Roy. Soc., vol. 64 (1898), pp. 130–142.
 A. Gautier, Comptes Rendus, vol. 132, pp. 58–64, 189–194.

granite powder together with a mixture of two parts of sirupy phosphoric acid and one part of water to only 100°, he received more than 10 times as much gas as was evolved at 300° without the acid, or about 1.5 volumes. Table 7 comprises Gautier's analyses of the gases expelled at red heat.

TABLE 7.

Rock.	H <sub>2</sub> 8.	CO <sub>2</sub> .	co.	CH <sub>4</sub> .	Hg.	N <sub>2</sub> .	Vol.
Granite, Vire I. Granite, Vire II Granite, Vire III Granitoid porphyry, Esterel. Ophite, Villefranque I Ophite, Villefranque III. Lherzolite, Lherz.	1.71 0.69 0.00 3.44 5.56 0.45	14.80 8.98 14.42 59.25 28.10 30.66 35.71 78.35	4.93 5.12 5.50 4.20 3.91 4.45 4.85 1.99	2.24 1.09 1.99 2.53 1.40 0.66 1.99 0.01	77.30 82.80 76.80 31.09 63.28 58.90 56.29 7.34	0.83 0.42 0.40 2.10 0.05 0.13 0.68 Trace	\begin{cases} \text{Av.} \ 6.9 \\ 7.6 \\ 7.60 \\ 15.7 \end{cases}

The rôle played by these gases in vulcanism, and their connection with thermal waters, is discussed in more recent papers.1 Following Gautier, Huttner<sup>2</sup> showed by a series of experiments that when a stream of dry carbon dioxide is passed over a rock powder at a temperature of 800°, carbon monoxide results, owing to a reduction of the dioxide, as this investigator believes, by some of the hydrogen given off from the rock. As the minerals orthite and gadolinite yielded no carbon monoxide, though abundant hydrogen, when gelatinized in hydrochloric acid, he came to the conclusion that this gas does not exist in rocks.

In 1905 there appeared a paper by Albert Brun, "Quelques Recherches sur le Volcanisme," based upon studies of lavas from Vesuvius, Stromboli, and other Mediterranean volcanoes. While no complete gas analyses were undertaken, much experimentation was done, covering the expulsion of gases and vapors at or near the fusion point of the lavas. This author expresses the opinion that it is the liquefaction of the rock which produces the gases, these being engendered by chemical bodies contained within the lava itself. The gases recognized are nitrogen and its derivative ammonia, chlorine with derived hydrochloric acid, and hydrocarbons. The nitrogen is assigned to nitrides, and the ammonia to reactions between nitrides and hydrocarbons, while a dissociation of chlorides furnishes free chlorine which may take hydrogen from hydrocarbons to form hydrochloric acid. source for hydrogen and carbon dioxide is recognized in hydrocarbon compounds, though Brun was less interested in the gases expelled below the melting-point of the lava.

<sup>Gautier, Comptes Rendus, vol. 132, pp. 740-746 and 932-938; Economic Geology, vol. 1 (1906), pp. 688-697.
K. Hüttner, Zeitschrift für Anorg. Chem., 43 (1905), pp. 8-13.
A. Brun, Archives des Sciences phys. et naturelles, Genève, 1905.</sup> 

#### METHOD OF PROCEDURE.

To obtain the gases for these investigations, the general methods of Graham, Mallet, and Wright were adopted, though the details of the apparatus were modified in many particulars. The gas is extracted from the rock material which has been finely pulverized, by heating the powder in a vacuum. For this purpose an apparatus consisting of a combustion-tube connected with a mercury-pump capable of producing and maintaining a vacuum of a fraction of a millimeter pressure is required. Simplicity being desirable in order to insure the uniform working of the pump in the presence of corrosive gases, such as hydrogen sulphide and sulphur dioxide, which attack and befoul the mercury, the most elementary type of Töpler¹ pump was used in these experiments.

To the receiving end of the pump a long, horizontal, calcium chloride drying-tube is fused. The ideal method would be to seal the combustion-tube containing the rock powder directly to the free end of this drying-tube. But inasmuch as the pump and drying-tube are both constructed of soft glass, whereas the tube in which the high-temperature combustions are to be made must, of necessity, consist of the most refractory glass, which can not be readily united to the fusible glass, one break in the system is unavoidable. This is made at the end of the drying-tube, which is ground so as to receive a tightly fitting hollow stopper of the same hard, blue Jena composition tubing as the combustion-tube. A 5-millimeter tube of blue Jena glass joins the combustion-tube to the stopper, and is taken of sufficient length to allow of repeated cutting and resealing to successive tubes, as they become useless from slow deformation under the combined influence of high temperature and vacuum.

influence of high temperature and vacuum.

The capillary exhaust-tube of the pump, dipping under mercury in a trough, is bent upward at its lower extremity, so as to deliver the gas expelled from the pump directly into the receptacle designed for holding it. For this purpose, a separatory funnel of about 125 cubic centimeters capacity, held by a clamp in an inverted position over the mercury trough, proved most serviceable.

In making an analysis, the rock specimen is first reduced to a powder of sufficient fineness to pass through a sieve of 30 meshes to the inch. A portion of this powder, roughly estimated to approach the maximum quantity which can with safety be placed in the combustion-tube, is then weighed and carefully poured into the tube through the hollow stopper, which, on account of its shape, serves as a funnel. Because the rock-dust in falling becomes somewhat packed, the tube must afterwards be held in a horizontal position, and gently shaken or tapped, to establish a free passageway for the gases, extending the entire length of the tube; otherwise, upon attempting to exhaust, preparatory to heating, the air entrapped in the powder, having no avenue of ready escape, will expand so rapidly as to force some of the material into the drying-tube.

Thus carefully filled, the tube is placed in the combustion-furnace, which stands upon a table of height such that the stopper end of the com-

Described by Travers, A study of gases, pp. 5-10.

bustion-tube meets approximately the ground end of the calcium chloride tube coming from the pump. The pump itself, installed upon a specially constructed table resting on jacks, can be raised or lowered, or tilted at a slight angle in any direction necessary to enable the stopper protruding from the furnace to fit exactly into the drying-tube. As the whole apparatus is now rigid glass from end to end, care is required in fitting the two parts together, lest there be strain sufficient to cause serious fracture. To prevent leakage during the extraction of the gas, the ground-glass connection (the only source of leakage) is completely incased in a thick coating of paraffine.1

The air in the apparatus is now pumped off until the exhaustion can be carried no further, at which point the pressure may be in the neighborhood of 0.01 millimeter. If allowed to stand for several days this vacuum remains entirely without change. When ready, the burners in the furnace are lighted, the separating funnel in which the gases are to be collected is filled with mercury, and the evolution of the gas is under way. As fast as the gases are liberated by the heat they are pumped over into the collecting-funnel—a process usually requiring about 3 or 4 hours before the last traces of gas have been expelled.

#### ANALYSIS OF THE GAS.

After constant temperature has been established in the room, the gas is drawn from the receiver into a Lunge nitrometer and the carbon dioxide and hydrogen sulphide absorbed by the introduction of a cubic centimeter of 30 per cent potassium hydroxide solution. The remaining gas is transferred to a gas-burette, filled with water, after which the remainder of the analysis is carried on according to the method described by Hempel.<sup>2</sup> From the potassium hydroxide solution the amount of hydrogen sulphide absorbed is determined by titration with N/100 iodine solution. If it be desired to measure the quantity of helium and argon, the gas remaining after the removal of all the constituents, except nitrogen and these inert gases, is passed over metallic calcium heated to redness.3 This absorbs the nitrogen, leaving only helium and argon, which are examined spectroscopically.

Whenever rocks containing a large proportion of quarts are tested, it is necessary to substitute a porcelain tube, since quarts scratches glass, causing it to crack when heated. The connections are readily made tight with paraffine.
 Hempel, Methods of gas analysis: Technical method.
 Travers, A study of gases, p. 102.

The analyses are numbered in table 8 in the order in which they were made, and therefore furnish a chronological account of these investigations. At the commencement of these studies, it being deemed advisable to make a rapid survey of the field and establish the range of the phenomenon, in order to direct later experiments more intelligently, less attention was given to securing the most trustworthy method of extracting the gas. Twenty-two analyses were made during the preliminary trial stage, before the apparatus was overhauled and sealed glass connections substituted for rubber tubing. As it was difficult to prevent a slight leakage of air into the tubes of the original apparatus, the first 22 analyses are characterized by a higher percentage of nitrogen than those made afterwards under more favorable conditions. Hydrogen sulphide was not determined in the first 17 analyses.

Table 8 gives the percentage of each gas in the total volume of gas; and the volume of each gas (at 0° and 760 mm. pressure) per unit-volume of rock.

TABLE 8.

Specimen No. and remarks.	Per cent or volume.	Hydrogen sulphide (HgS).	Carbon dioxide (CO <sub>2</sub> ).	Carbon monoxide (CO).	Methane (CH4).	Hydrogen (H2).	Nitrogen (N2).	Total.
<ol> <li>Medium-grained white granite, rather low in quartz.</li> <li>Very coarse granite with prominent pink feldspar phenocrysts.</li> <li>Keewatin schist from Mesabi district, Minn. From oldest known series of Lake Superior region, highly carbonated. (Specimen 40896, Slide 15466, U. S. G. S.) From C. R. Van Hise.</li> </ol>	P. ct. Vol. P. ct. Vol. P. ct. Vol.	:::: :::: :::::	19.20 .28 11.56 .42 63.76 7.67	4.94 .07 2.41 .09 2.33 .28	4.85 .07 2.70 .10 .43 .05	64.01 .92 80.29 2.94 31.66 3.82	7.00 .10 3.04 .11 1.82 .22	100 1.44 100 3.66 100 12,04
<ol> <li>Laurentian dike rock from Lake Superior. (Specimen 41879, Slide 16673, U. S. G. S.) Gneiss from contact of Keewatin green- stone and Laurentian granite near Rat Portage, Ont. From C. R. Van Hise.</li> </ol>	P. ct. Vol.	322	14.74	3.93	2,85	71.88 1.50	6.60	100 2.08
5. Kinderhook shale. Burlington, Iowa.	P. ct.		91.65	3.46	1.24	2.18	1.47	100
From Stuart Weller.  6. Portage shale, Ithaca, N. Y. From Dr. Weller. (Nitrogen omitted from analy-	Vol. P. ct. Vol.	::::	9.28 39.80 1.47	.35 22,65 .83	4.25 .16	33.30 1.23	.15	10,12 100 3,69
sis because of leakage of air into tube.)  7. Muscovite, Canada; material taken from a large slab of mica in Walker Museum collection.	P. et. Vol.		70.33 1.26	6.59	2.74	5.49 .10	14.85 .27	100 1.79
8. Potsdam sandstone, Baraboo, Wis. Treat- ed with HCl to remove any carbonate from the surface of the grains.	P. ct. Vol.	****	45.70 .47	17.19 .18		78 01	36.32 .38	100 1.04
9. Pike's Peak granite, from carriage-road across divide between N. Cheyenne and Bear Creek canyons. A coarse-grained, yellowish-pink granite constituting the great mass into which the finer-grained pinkish granite of the peak proper has been intruded.	P. ct. Vol.	****	60.74	9.24 .05	2.70	6.47	20.85	100
10. Rhyolite, Marble Mountain on north slopes of San Francisco Peaks, Ariz.	P. ct. Vol.	8164	44.15 .22	16.40	7.14	5.81	26.50	100
11. Keweenawan diabase, from 1 mile east of Dresser Junction, Polk Co., Wis. (a lava flow).	P. et. Vol.	2	12.05	.93	3.83	78.14 3.83	5.05	100 4.91
12. Quartzite schist, collected 2 miles south-	P. et.	****	46.05	20.68	7.93	7.29	18.05	100
west of Baraboo, Wis.  13. Andesite. Silver Creek Basin, Ouray Co.,	P. ct.		.16	36.28	7.61	27.91	.06 28.20	100
Colo. 14. Coarse porphyry from dump pile of San	Vol. P. ct.	****	(i)	.09 16.15	7.51	73.00	.08 3.34	100
Pedro Mine, Ouray Co., Colo.	Vol.	,	(.)	.05	.02	.22	.01	.50

<sup>1</sup> Carbonated.

TABLE 8-Continued.

	Specimen No. and remarks.	P. ct. or vol.	H <sub>2</sub> 8.	003.	co.	CH <sub>4</sub> .	H <sub>2</sub> .	Ng.	Total.
16.	Gabbro diorite from about 13,000 ft. eleva- tion on south side of Mt. Sneffels, Colo. Coarse-grained gabbro diorite, summit of Mt. Sneffels, Colo. Coarse orthoclase gabbro from bluff about 100 paces east of the "Favilion," in N. 3 sec. 28, Duluth, Minn. Specimen 4602,	P. ct. Vol. P. ct. Vol. P. ct. Vol.		22.01 .40 (¹)  12.08 .44	5.54 .10 10.08 .12 8.20 .12	2.05 .04 1.92 .02 1.79 .07	62.88 1.13 79.15 .97 78.95 2.68	8.07 .14 8.85 .11 8.97 .82	100 1.81 100 1.22 100 8.68
18.	Slide 4602, U. S. G. S. This belongs to the St. Louis River series (6000 ft. thick) which is the lowest member of the Keweenawan at Duluth. Collection of R. D. Irving. References: Monograph v. U. S. G. S., pp. 50-53, 266, and 268-275. Hamilton shale, along the Susquehanna, 1 mile south of Marysville, Pa.; a very	P. ct. Vol.	0.04 .00	16.52 .41	6.91 .17	2.90 .07	57.89 1.45	15.75 .40	100 2,50
2419	hard indurated shale.  Massive granite porphyry, Horse Race, near Upper Quinnesec Falls, Menominee district. Specimen 11082, Slide 5700, U. S. G. S. Collection G. H. Williams.	P. ct. Vol.	::::	51.26 8.51	10.55 .72	.86 .06	84.19 2.84	8.14 .22	100 6.85
<b>420.</b>	Fine-grained gneiss, same rock-mass as No. 19. Specimen 11085, Slide 5702, U. S. G. S. Collection G. H. Williams.	P. ct. Vol.	.24 .00	67.24 1.89	8.81 .28	.79 .02	14.96 .48	8.46 .28	100 2.80
<b>421.</b>	Fine-grained banded gneiss, same rock- mass as Nos. 19 and 20. Specimen 11084, Slide 5701, U. S. G. S. Collection G. H. Williams.	P. ct. Vol.	::::	71.47 6.68	12.20 1.18	.68 .06	14.75 1.87	.90 .08	100 9.27
22,	Laurentian granite, Marquette district, Mich. Specimen 14392, Silde 9259. From C. R. Van Hise.	P. ct. Vol.	::::	64.41 1.89	4.41 .18	.98 .08	25.15 .74	5.10 .15	100 2.94
28.	Schist with chloritoid, Black Hills, S. Dak. Specimen 14928, Slides 7671, 14968, and 14969. References, Bull. 239, pl. XIV. Described by Van Hise, Bull. G. S. A., vol. 1. Developed by anamorphism of graywacke-slate series through the influence of batholithic granite.	P. ct. Vol.	::::	12.49 .46	2.56 .10	1.10 .04	82.58 8.07	1.82 .05	100 8.72
24.	fluence of batholithic granite.  Pink orthoclase granite, North Carolina.  Obtained from Blake & Co., marble cutters, Chicago.	P. ct. Vol.	.18 .00	28.86 .16	8.28 .06	8.88 .02	57.31 .38	6.59 .04	100 .65
25.	Dark olive-gray granite, Quincy, Mass. From Blake & Co.	P. ct. Vol.	.10 .00	24.56 .89	5.48 .09	8.40 .06	64.84 1.04	1.62	100 1.60
<b>€26.</b>	Fine-grained gray granite, Russia. From Blake & Co.	P. ct. Vol.	.08 .00	60.48 1.79	6.15 .18		88.86 .99		100 2.96
27.	Baltimore gneiss, Williams' quarry, Roberts Road, 2 miles west of Bryn Mawr,	P. ct. Vol.	.01 .00	2.95 .18	2.05 .10	2.99 .14	91.11 4.32	.89	100 4.78
28.	Pa. From F. Bascom. Baltimore gneiss, Schuylkill River section, 1 mile SE. of Spring Mill, Pa. From F.	P. ct. Vol.	4.91 .80	22.17 1.85	8.69 .22	1.74 .11	65.85 4.02	1.64 .10	100 6.10
29.	Bascom. Wissahickon mica gneiss, Fovelton's quarry, on Childs estate, 2 miles SW. of Bryn Mawr, Pa. From F. Bascom.	P. ct. Vol.	.58 .00	19.07 .19	6.67 .07	2.21 .02	67.88 .65	4.19 .04	100 .97
<b>80</b> .	ry, W. bank of Schuylkill River. A more solid, compact rock than No. 29, which	P. ct. Vol.	.06 .00	8.26 ,19	8.85 .06	3.50 .08	81.65 1.90	8.18 .08	100 2.83
81.	was sericitic. From Dr. Bascom. Cambrian gneiss, West Grove Ridge, Costeville Quadrangle, Pa. From Dr. F. Bascom. Resembles an impure and- stone whose argillaceous material had been altered to mice during the meta- morphic process; crushes to a sandy powder like a sandstone.	P. ct. Vol.	••••	88.99 .26	11.43	1.21 .01	49.02 .87	4.36 .08	100 .76

<sup>1</sup> Carbonated.

2 No. 17. Analysis (by Strong): SiO<sub>b</sub> 49.15; Al<sub>2</sub>O<sub>b</sub> 21.90; Fe<sub>2</sub>O<sub>b</sub> 6.60; FeO, 4.54; CaO, 8.22; MgO, 8.08; Na<sub>2</sub>O, 8.88; K<sub>2</sub>O, 1.61; H<sub>2</sub>O, 1.92; 100.80.

2 No. 19. Analysis (Riggs, Bull. 62, p. 118): SiO<sub>b</sub> 54.88; Al<sub>2</sub>O<sub>b</sub> 25.49; Fe<sub>2</sub>O<sub>b</sub> 1.61; FeO, 1.65; CaO, 6.06; MgO, 1.96; Na<sub>2</sub>O, 5.69; K<sub>2</sub>O, 1.87; H<sub>2</sub>O, 1.18; CO<sub>c</sub>, 1.8; 100.64.

4 Nos. 19, 20, and 21 were collected from an intrusion of granite-gneiss into greenstone, which has been called Upper Huronian by Brooks, the granite-gneiss being placed at the top of the Upper Huronian. Bulletin 62, p. 26. This series shows a gradation from massive porphyritic granite to very fine-banded gneiss. No. 19 is from the center of the intrusive dike, and grades almost imperceptibly on both sides into the fine-grained gneiss of which No. 20 is the type. No. 21 is similar to No. 20, being on the sides, but is banded. This rock is more basic than typical granite, being more like a diorite in composition. The low gas-volume of No. 20 in comparison with the two other specimens is perhaps to be explained by the fact that it is a much more porous rock, crumbling readily to a fine powder on the anvil.

5 Owing to an accident during the explosion it was impossible to determine the relative amounts of CH<sub>4</sub>, H<sub>6</sub>, and N<sub>2</sub>, but the violence of the explosion suggests that there was little N<sub>2</sub> present.

TABLE 8-Continued.

	Specimen No. and remarks.		P. ct. or vol.	H	8.	CO <sub>2</sub> .	<b>c</b> 0.	CH	4-	Hg.	N <sub>2</sub> .	Total.
182.	Olivine free, saussuratized schistose bro, Menominee district, Lake Sup- region. Specimen 11166, Silde 5747. scribed by Williams, Bull. 62, pp. 6 An extremely altered gabbro, con- ing calcite, sericite, chlorite, and	De- 2-76. tain-	P. ct. Vol.	0.0		57.50 20.07	1.96 .58	0.6		8.71 8.54	1.08 .82	100 29.78
83.	coxene. Laurentian gneiss, Marquette dist Mich. Specimen 14718, 81de 9861, G. S. From C. R. Van Hise.	- 1	P. ct. Vol.	.o.		28.81 .85	5.07 .15	2.6		9.66 1.79	4.25 .12	100 2.98
84.	Cewatin greenstone, Messoi dist Oldest known series of the Lake Si ior region. Specimen 40785, Slide Ii U. S. G. S. Considerable water	per- 5420, was	P. ct. Vol.	.5	8 6	32.38 20.08	8.60 1.16	.21	8 8	1.98 0.10	1.78 .57	100 82.19
85.	given off when powder was her From C. R. Van Hise. Keweenawan diabase, railroad cut s	outh	P. ct. Vol.	.4	5	7.05	1.57 .06	1.7		7.66	1.50	100 3,59
86.	of schoolhouse in Taylor's Falls, M Olivine gabbro, from foot of cliff at headland of Beaver Bay, near Dul Minn. Specimen 4601, Slide 4601, U. S. Collection R. D. Irving. (Referer Mon. v, U. S. G.S., Lithol., pp. 37-45.	NE. luth, S.G.	P. ct. Vol.	.0	6 ]	.16	7.91 .07	.00 8.90 .00	5 6	8.15 2.54 .52	.06 5.16 .05	100 .84
87.	cation on map, p. 305; description, p. Oglesby blue granite, near Elberton bert Co., Ga. From S. W. McCallie	.309.	P. ct. Vol.	.0	7 4	17.06 1.18	4.74 .11	1.57		4.28 1.06	2.28 .05	100 2.88
88.	De Kalb Co., Ga. From S. W. McCa	tain, allie.	P. ct. Vol.	.1	0   1	.08	4.85 .08	1.50	5 7	7.20 .60	5.87 .04	100 .76
	Coarse reddish Archean granite, Stone Lake, near Ortonville, M From Blake & Co. Microcline orthoclase form large crystals; qu is abundant, but blottie is rather sp Described in Geol. of Minn., vol. 5, p Ortonville granite, blottie crystals of specimen separated from quartz	and artz arse. .814.	P. ct. Vol.	1.6 .2	1 1	97.84 1.20 92.40	8.51 .05	1.16 .01	5	2.23 .30	3.83 .05	1.86 1.86 100 13.47
	feldspar by mercuric iodide spe gravity solution.	cific	<b>VO1.</b>									20.11
	Specimen No. and remarks.	Per cent or volume.	Hydrogen sulphide (H <sub>2</sub> S),	Нудгосагров уароги	Sulphur dioxide (SO <sub>2</sub> ).	Carbon dioxide (00 <sub>2</sub> ).	Carbon monoxide (CO).	Heavy hydrocar- bons.	Methane (CH,).	Hydrogen (H2).	Nitrogen (N2).	Total.
41.	Hamilton shale, Newsom's Station, 15 miles W. of Nashville, Tenn. From Miss Augusta T. Hasslock.	P. ct. Vol.	30.94 29.38	::::	::::	21.17 20.10	4.61 4.38	4.29 4.07		38.99 37.03		100 94.96
142, 143.	An exceedingly bituminous shale emitting a strong odor resembling that of asphalt when struck with a hammer. What part of this gas really existed within the rock in the gaseous state can not be stated; most of it probably came from decomposition of organic matter present. Heavy brown tars also produced. No determination of hydrocarbon vapors was made. Oil-rock from lead-zinc mine near Platteville, Wis. From H. F. Bain. Sillimanite gneiss, St. Jean de Matha, Quebec. From F. D. Adams.	P. et. Vol. P. et, Vol.	6.79	11.11 6.88	54.74 2.76	18.12 10.43 40.55 2.05	8.40 4.82 1.64	4.00 2.30	35.98 20.67 .61 .03	13.18 7.57 1.10 .05	2.16 1.24 1.36 .07	100 57.46 100 5.05

<sup>&</sup>lt;sup>1</sup>No. 22. Analysis: SiO<sub>3</sub>, 28.05; Al<sub>2</sub>O<sub>3</sub>, 24.78; FeO, 5.65; Fe<sub>2</sub>O, 6.08; CaO, 1.25; MgO, 11.58; Na<sub>2</sub>O, 2.54; K<sub>2</sub>O, 1.94; H<sub>2</sub>O, 7.53; CO<sub>3</sub>, 0.53; 100.28. (R. B. Rigga, Bull. 62, p. 76.)

<sup>9</sup> Probably only a small part of gas was really present in the gaseous condition, the analysis being made to show what a bituminous shale may yield.

<sup>3</sup> A metamorphosed slate of the Grenville series. Reference: Am. Jour. Sci., vol. 50, p. 88. Described as a fine-grained garnetiferous sillimanite gneiss containing much quarts and orthoclase. Graphite and pyrite also present, causing the gneiss to weather to a very rusty color. Analysis by N. N. Evans, of McGill University: No. 45. SiO<sub>4</sub>, 51O<sub>5</sub>, 1.63; Al<sub>2</sub>O<sub>5</sub>, 19.73; Fe<sub>2</sub>O<sub>5</sub> and FeO, 4.60; FeS<sub>3</sub>, 4.38; MnO, trace; CaO, 0.38; MgO, 1.81; Na<sub>2</sub>O, 0.79; K<sub>2</sub>O, 2.50; H<sub>2</sub>O (ignition), 1.82; 99.55.

TABLE 8—Continued.

Specimen No. and remarks.	Per cent or volume	Hydrogen sulphide (H <sub>2</sub> S).	Carbon dioxide (CO <sub>2</sub> ).	Carbon monoxide (CO).	Methane (CH4).	Hydrogen (H <sub>2</sub> ).	Nitrogen (N <sub>2</sub> ).	Total.
44. Nephelite syenite, north of Mountain Lake, Tp. of Methuen, Ontario, F. D. Adams.	P. et. Vol.	::::	42.42 ,29	8.76 .05	5.49 .04	36,33 .25	7.00	100
Of igneous origin. 45. Iron-bearing basalt, Ovifak, Disco Island, Greenland.	P. ct. Vol.	0.03	46.50 3.74	21.63 1.74	2.09	27.88 2.24	1.87	100 8.05
46. Magnetite sand, Snake River bed, Idaho, from Oskar Eckstein. Separated from	P. ct. Vol.	****	83.91 2,22	10.19 .27		5.90 .16		100 2,65
impurities by magnet.  47. Andesite, Red Mountain, NW. of San Francisco Peaks, Ariz. Collected by W. W. Atwood. Mr. Arthur Taylor describes this rock as an andesite porphyry whose ground-mass (96 p. ct. of the whole) consists of 48 p. ct. pyroxene, 31 p. ct. plagiociase (labradorite), and 12 p. ct. magnetite. The phenocrysts are lime-soda feldspar, augite, hornblende, and magnetite. Occurs as irregular blocks cemented in the tuff or volcanic breccia of	P. ct. Vol.	.01	80.38 5.12	9.02	4.74	1.84	4.03	100 6.37
which Red Mountain is built.  48. Pyroxene crystals, Red Mountain, Ariz. Collected by W. W. Atwood. These crystals, ranging in size from a bean to a small marble, were found loose on the surface, having weathered out of the breccia.	P. ct. Vol.	8.90 .10	62.62	14.46 .16	1.30	7.01	5.71	1.10
<ol> <li>Rhyolite vitrophyre, ridge N. of Park Basin, Telluride Quadrangle, Colo. Specimen No. 3054 U. S. G. S. A lava flow belong- ing to the intermediate series. From</li> </ol>	P. ct. Vol.	::::	92.66 2.33	1.94 .05	1.39	2.71	1.30	100 2,51
Whitman Cross.  50. Nephelite melilite basalt, Uvalde Quadrangle, Tex. Collected by T. W. Vaughan. Described (Uvalde Folio, p. 4) as a very fine-grained, dark-colored rock, with the nephelite invisible to the naked eye. Contains little or no feldspar and comparatively little nepheline. Olivine and aughte are the most important constituents. The presence of melilite indicates unusual amount of lime in magma. Age	P. ct. Vol.	1.99	40.32 1.07	7.55	2.18	44.18 1.16	3.78 .10	100 2.64
doubtfully placed as Eocene.  51. Shonkinite, Highwood Mountains, Mont. Core rock of Shonkin stock. Described (Ft. Benton Folio, p. 3) as a rock of the syenite family very rich in augite, con- taining accessory olivine and black mica. While the chief light-colored constituent is orthoclase, nephelite and sodalite are present in varying amounts. An intru- sive of probably Eocene age. Collected by W. H. Weed.	P. et. Vol.	.04	8.85	4.97	8.94 .05	78.08 .95	4.12	1.22
52. Theralite, from the laccolites on Upper Shield River Basin, Crazy Mountains, Mont. U. S. National Museum No. 73138. Collected by W. H. Weed. Described (Little Belt Mountains Folio, p. 4) as a dark-gray basaltie rock commonly occurring in sheets, but rarely in dikes. Porphyritic crystals of augite form the most prominent phenocrysts, though large plates of brown mica are common. Colorless part of the ground-mass is a granular mixture of nephelite and lime-soda	P. et. Vol.	.00	48,18 1.08	7.63	1.58	41.21	1.39	100 2.25
feldspars. Eocene age.  58. Quartz syenite porphyry, summit of Engineer Mountain, Silverton Quadrangle, Colo. No. 3728 U. S. G. S. From Dr. Cross. Described (Silverton Folio, p. 11) as strongly porphyritic, with many glassy orthoclase crystals colored reddish by fine	P. ct. Vol.	::::	(1)	24.89 .11	17.22	50.22	7.53	100

<sup>&</sup>lt;sup>1</sup> Carbonated.

TABLE 8—Continued.

Specimen No. and remarks.	P. ct or vo		<b>.</b> 8.	CO <sub>2</sub> .	<b>co</b> .	СН	4	H <sub>2</sub> .	Ng.	Total
ferritic pigment. Also phenocrysts of quarts, pisgioclase, biotite, and horn- blende; dark, ash-gray ground-mass. Either an intrusive or resting upon andes- itic tuffs of Silverton series. 54. Altered Jurassic shale, LaPlata Quadrangle, Colo. Contact zone below Indian Trail Bidge. Alteration due to intrusion of vogesite. (See analysis No. 84.) From Dr. Cross.	P. ct. Vol.		00	(a) 	22.09	5.4	•	5.96	6.28	100
<ol> <li>Garnetiferous gneiss, Darwin's Falls, Tp. of Rawdon, Quebec. Probably of sedi- mentary origin. From F. D. Adams.</li> </ol>		-	11	20.26 .16	9.51 .07	2.1	2	2.20 .41	2.65 .02	100 .79
<ul> <li>56. Hornblende syenite, Cape Elisabeth, Me. From the drift. U. S. N. M. NO. 80685.</li> <li>57. Granite porphyry bowlder, northern New York.</li> <li>58. Intrusive in Highwood Mountains, E. side of divide, Highwood Gap, Ft. Benton Quadrangle, Mont. Microscopically resembles a diorite; probably of Eocene age. Collected by W. H. Weed.</li> </ul>	P. ct. Vol.	8.	04	6.18 .16 (¹) 81.91 .28	2.76 .07 22.19 .27 8.44 .07	1.00 .00 1.77 .00 4.4	5 6 2 5	8.77 2.22 9.87 .85 1.25	1.28 .03 8.34 .04 8.96 .08	100 2.50 100 1.22 100 .87
age. Collected by W. H. Weed.  159. Nevadite, Chalk Mountains, Ten-mile district, Colo. From U. S. Nat. Mus. Described in Monograph XII, p. 345. Contains numerous dark quarts crystals and clear sanidines, embedded in a light gray ground-mass made up of sanidine, plagioclase, and quartz, but containing little biotite or magnetite.	P. ct. Vol.			57.19 -15	19.29 .06	4.70		7.58	11,28 .08	100 .27
Specimen No. and remarks.	Per cent or volume.	Hydrogen sulphide (H <sub>2</sub> S).	Sulphur dioxide (SO2).	Heavy hydrocar- bons.	Carbon dioxide (CO <sub>2</sub> ).	Carbon monoxide (CO),	Methane (CH.).	Hydrogen (H2).	Nitrogen (Ng).	Total.
<ol> <li>Diorite plug in Cretaceous shales, between forks of Deep Creek on ridge from Mt. Ruffner, 3 miles from lower contact, Tell- uride Quadrangle, Colo. No. 2872 U. S. G. S. From Whitman Cross.</li> </ol>	P. ct. Vol.	2.06	::::	0.16	14.55 ,22	4,18	3.41	71.37 1.10	4.27	100 1.52
<ol> <li>Diabase, Nahant, Mass.</li> <li>Andesite, Rosita Hills, Custer Co., Colo., from summit of small hill east of spring on Rosita Road. Dike facies of Pringle</li> </ol>	P. et. Vol. P. et. Vol.	2.18 .19 .06 .00	::::		56.58 4.91 (1)	2.36 .21 85.67 .27	1.36 .12 6.67 .05	35.93 3.13 40.02 .30	1.64 .15 17.58 .13	100 8.71 100 .75
type. (See report on Geology of Silver Cliff, Rosita Hills area, by Whitman Cross.) 63. Anorthosite, sheared igneous rock, 2.5 miles from Chertsey, Quebec. F. D. Adams. 64. Andesite, Lipari Islands.	P. et. Vol. P. et. Vol.	.02 .00 .06 .00			71.99 2.36 70.29 .56	8.40 .27 4.85 .04	.54 .02 .98 .01	17.17 .56 21.62 .17	1.88 .06 2.20 .02	100 3,27 100 .80
65. Fine-grained gneiss, lot 5, Concession I, Harburn Tp., Ontario. Dr. Adams re- gards this as almost certainly an altered sediment, for it occurs in beds interstrati- fied with limestone. Impregnated with pyrite and contains graphite. Analysis shows it to be a tehanose.	P. et. Vol.	::::	85.12 4.15		13.89	_		.99		100 4.88
shows it to be a tehamose. 66. Gneiss of igneous origin, lot 28, R. 9, Wollaston Tp., Ontario. F. D. Adams. 67. Feather amphibolite, lot 16, R. 12, Wollaston Tp., Ontario. Probably of sedimentary origin. F. D. Adams.	P. ct. Vol. P. ct. Vol.	.04 .00 .22 .00	:::	:::	19.35 .28 (¹)	8.91 .13 54.45 .49	2,20 .03 2,89 .03	64.24 .95 35.62 .32	5,26 .08 6,82 .06	100 1.47 100 .90

<sup>&</sup>lt;sup>1</sup> Carbonated. <sup>2</sup> No. 59. Analysis (p. 589): SiO<sub>2</sub>, 74.45; Al<sub>2</sub>O<sub>2</sub>, 14.72; FeO, 0.56; MnO, 0.28; CaO, 0.38; MgO, 0.37; K<sub>2</sub>O, 4.58; Na<sub>2</sub>O, 8.97; H<sub>2</sub>O, 0.66; P<sub>2</sub>O<sub>3</sub>, 0.01; 100.38.

TABLE 8—Continued.

	Specimen No. and remarks.	Per cent or volume.	Hydrogen sulphide (H <sub>2</sub> S).	Carbon dioxide (CO <sub>2</sub> ).	Carbon monoxide (CO).	Methane (CH4).	Hydrogen (H2).	Nitrogen (N <sub>2</sub> ).	Oxygen (O <sub>2</sub> ).	Total.
68.	Amphibolite, Maxwell's Crossing, Glamor- gan Tp., Ontario. A highly altered lime-	P. et. Vol.	0.06	(1)	10.94 .26	2.11	84.01 2.01	2.88 .06		100 2.38
69.	stone. Dr. Adams. Rice rock, Canadian Pacific R. R. 0.25 mile east of Sudbury, Ontario. Probably an altered sediment of Huronian age. Dr.	P. ct. Vol.	4.86 .16	14.67 .47	5.14 .16	1.45 .05	71.89 2.32	1.99 .06	::::	100 3,22
70.	Adams. Andesite, Granite Mountain, Iron Co., Utah. A laccolite in Paleozoic sediments. C. K. Leith.	P. ct. Vol.	.03	77.50 2.66	4.75 .16	.95 .03	15.35 .53	1.42 .05	****	100 3.43
71.	Vein quartz, Granite Mountain, Iron Co., Utah. Associated with iron ore which has developed along the contact of the laccolite and intruded limestone. Accord- ing to Leith it was presumably derived from the andesite (No. 70).	P. et. Vol.	::::	13.93	11.26 .09	4.00	64.40 .53	6.41		100
72.	Phonolite trachyte, east part of Bull Mountain, Pike's Peak Quadrangle, Colo. No. 2488 U.S. G.S. Described by Cross (Pike's Peak Folio, p. 3) as a dense, grayish-green rock with tabular crystals of sanidine, which give it a typical porphyritic texture.	P. ct. Vol.	.27	69.37 .76	4.85	2.67	17.16 .19	5.69	140	100 1.08
73.	Coarse diorite bowlder from Bluehill sheet, Penobscot Bay Quadrangle, Me. From	P. ct. Vol.	3.28	14.99 .27	3.78 .07	2,00 .04	72.83 1.29	3,12 .05	100	100 1.78
74.	E. S. Bastin. Diorite, Deer Isle sheet, Penobscot Bay Quadrangle, Me. No. 1157. From E. S.	P. ct. Vol.	1.44	4.65 .21	.78 .04	4.38	85.62 3,95	3.13 .14	3-93	100 4.61
75.	Bastin.  Potsdam sandstone, upper narrows of the Baraboo, Ablemans, Wis. Hard, indurated white sandstone, not far from the contact with the quartzite.	P. ct. Vol.	.15 .00	27.29 .09	15.12 .05	5.88	37.86 .13	13.70 .05	2502 2001	100 .34
	Potsdam sandstone, Ablemans, Wis	P. ct. Vol.	.08	9.67 .05	15.42	3.70	52.11 .23	19.02	141.1	100
	Huronian quartzite, South Range, near Bar- aboo, Wis.	P. et. Vol.	.13	25.12 .11	9.53	2.71	55.43	7.08		100
78.	Permian red sandstone, Garden of the Gods near Colorado City, Colo.	P. ct. Vol.	.05	(1)	60.69	6.27	27.28	5.71		100
79.	Gods, near Colorado City, Colo.  Topaz quartz-porphyry, Schneckenstein, near Auerbach, Saxony.	P. ct. Vol.	trace	33.41	8.16	4.87	45.40	8.15	****	100
80.	St. Peter sandstone, Minnehaha Creek, be- low the falls, Minneapolis, Minn. A soft, remarkably white, coarse-grained sand- stone. Before heating in the tube the grains were washed with dilute HCl.	P. ct. Vol.	2.6	56.5	9.6	15.7	1.7	13.9	:	100.97
81.	St. Peter sandstone, Minnehaha. The sand No. 80, pulverized and heated a second time.	P. ct. Vol.		6.40	13.73 .07	2.41 .01	35.19 .17	42.27 .21	****	100
82.	Quartzite belonging to Grenville Series, Darwin's Falls, Rawdon Tp., Quebec. From F. D. Adams.	P. ct. Vol.	37.65 .23	35.05 .21	7.12 .04	2.31 .01	15.60 .09	2.27 .01		100
83.	Quartz crystals, Lincoln Co., N. C. Beautiful crystals whose perfectly formed faces indicated that they were formed from aqueous solution. Entirely transparent and without visible inclusions.	P. et. Vol.	1.7	30.0	7.2	6.4	14.4 .01	35.1 .03	5.2	100
J84.	Vogesite, Indian Trail Ridge, La Plata Quadrangle, Colo. (a sheet in the Gunnison shales). A fine-grained greenish rock containing about equal amount of feld-spars and femle minerals, and more augite than hornblende; feldspars much sericitized and obscured by chlorite, epidote, and calcite. Described in La Plata Folio, p.7. From Dr. Cross. Allied type analyzed by W. F. Hillebrand.	P. ct. Vol.	Undet	(1)	10.58	2.48	82.53 1.08	4.41	****	1.30

<sup>&</sup>lt;sup>1</sup> Carbonated.

<sup>8</sup> The identical sand used in No. 75, powdered, and heated a second time. This experiment was to determine whether gas which was unable to escape might not still remain within the sand grains. As this powder yielded more gas than the fresh sand, most of the gas in the first trial apparently came from the surface of the grains.

<sup>8</sup> No. 84. Analysis: SiO<sub>2</sub>, 43.96; Al<sub>2</sub>O<sub>3</sub>, 13.30; Fe<sub>2</sub>O<sub>3</sub>, 3.67; FeO, 6.92; MgO, 7.08; CaO, 10.66; Na<sub>2</sub>O, 2.15; K<sub>2</sub>O, 1.64; H<sub>2</sub>O, 1.94; TiO<sub>3</sub>, 1.18; CO<sub>3</sub>, 6.46; P<sub>2</sub>O<sub>6</sub>, 32; FeS<sub>3</sub>, .54; etc. .36; 100.15.

#### TABLE 8-Continued.

Specimen No. and remarks.	P. ct. or vol		. o	02.	ю.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	02.	Total.
85. Keweenawan diabase; drill core from Franklin Junior Hole No. 8, near Houghton, Mich. From A. C. Lane. This piece came from a depth of 524 feet, measured along a line 49° from the horisontal. Overlaying drift amounts to 110 feet, so that the preglacial covering of specimen was in the neighborhood of 315 feet, plus thickness of rock removed by glaciers. This specimen is from a massive flow of ophite, 62 feet in thickness.	P. ct. Vol.			.61 2	2.40	2.85	60.24 2.84	1.87 .05	::::	100 3.88
<ol> <li>Diabase, Nahant, Mass. Material from same specimen as No. 61.</li> </ol>	P. ct Vol.	.0	0 8	.51	.84	1.82	88.69 4.68	1.28	••••	100 13.88 100
<ol> <li>Diabase, Nahant, Mass. Material from same specimen as No. 86.</li> <li>Balletian States St</li></ol>	P. ct Vol. P. ct		.	.06	.05 .05	6.36 .01 8.96	.05 83.80	27.05 .06 1.75	••••	100 .23
specimen as Nos. 86 and 87. 89. Albite crystals, Hebron, Maine	Vol. P. ct		1	.62	.14 1.06	.06 6.80	.54 49.95	.08 12.10	••••	1.60 100
<ol> <li>Wollastonite, Harrisville, Lewis Co., N. Y. Taken from a large specimen of pure- white wollastonite and reduced to a pow- der in an agate mortar. No suggestion of any iron. Acid liberated very little car-</li> </ol>	Vol. P. ct Vol.	.	.   87	.18	.18	.85 .02	2.16 .06	8.09 .08	••••	100 2.71
bon dioxide from powder. Walker Muse- um Collection. 91. Andesite, summit of Mt. Orizaba, Mexico,	P. ct	.			3.28	2.46	8.94	10.25		100
18,800 ft. altitude. Unquestionably a lava,	Vol.			.22	.05			.08		.31
and not a tuff, somewhat porous, giving off bubbles when immersed in water.  492. Amphibolite, Chester, Mass. A very coarse-grained specimen. Walker Museum.  492a. As the gas was still coming off slowly at the end of 5 hours, the same material was heated the next day for an additional 32 hours.	P. ct Vol. P. ct Vol.		36 2 7	.59 1'	7.13 1.05 3.65 .05	.00 1.57 .09 4.62 .01	.01 42.98 2.59 66.96 .25	1.78 .10 7.22 .08		100 6.08 100 .87
and not a tuff, somewhat porous, giving off bubbles when immersed in water.  492. Amphibolite, Chester, Mass. A very coarse-grained specimen. Walker Museum.  492a. As the gas was still coming off slowly at the end of 5 hours, the same material was heated the next day for an additional 32	P. ct Vol. P. ct		36 2 7	.59 1° .20 1°	7.18 1.06 3.65	1.57 .09 4.62 .01	42.98 2.59 66.96	1.78 .10 7.22		100 6.08 100
and not a tuff, somewhat porous, giving off bubbles when immersed in water.  492. Amphibolite, Chester, Mass. A very coarse-grained specimen. Walker Museum.  492a. As the gas was still coming off slowly at the end of 5 hours, the same material was heated the next day for an additional 3½ hours.  Specimen No. and remarks.  93. Pitchblende, Beaver Co., Colo. From H. N. McCoy.  194. Carnotite, Colorado, from H. N. McCoy.  Uranyi vanadate, probably with some	P. ct Vol. P. ct Vol.	nlphide	36 2 7	.59 .20 .55 .03	7.18 1.06 3.65 .06	1.57 .09 4.62 .01 .01 .03 .71	42.98 2.59 66.96 .25 ( <sup>7</sup> H) usboupAH 7.166 .07 1.48	1.78 .10 7.22 .03	(He).	100 6.08 100 .87
and not a tuff, somewhat porous giving off bubbles when immersed in water.  192. Amphibolite, Chester, Mass. A very coarse-grained specimen. Walker Museum.  192a. As the gas was still coming off slowly at the end of 5 hours, the same material was heated the next day for an additional 32 hours.  Specimen No. and remarks.  193. Pitchblende, Beaver Co., Colo. From H. N. McCoy.  194. Carnotite, Colorado, from H. N. McCoy. Uranyl vanadate, probably with some radium.  195. Greenalite rock, Blwabik formation, Messbi district, Minn. No. 46759 U. S. G. S.	P. et. Vol. P. et. Vol. P. et. Vol. P. et. Vol. P. et.	Hydrogen sulphide (H <sub>2</sub> S).	Sulphur dioxide (SO <sub>2</sub> ).	Carbon dloxide (0.09).	7.18 1.06 3.65 3.65 (00).	1.57 .09 4.62 .01 Wethane (CH)	42.98 2.59 66.96 .25 7.16 0.07 1.48 .06	1.78 .10 7.22 .03		100 6.08 100 .87
and not a tuff, somewhat porous, giving off bubbles when immersed in water.  192. Amphibolite, Chester, Mass. A very coarse-grained specimen. Walker Museum.  192a. As the gas was still coming off slowly at the end of 5 hours, the same material was heated the next day for an additional 32 hours.  Specimen No. and remarks.  93. Pitchblende, Beaver Co., Colo. From H. N. McCoy.  194. Carnotite, Colorado, from H. N. McCoy.  Uranyl vanadate, probably with some radium.  95. Greenalite rock, Biwabik formation, Mesa-	P. ct. Vol. P. ct. Vol. P. ct. Vol. P. ct.	12 000 Hydrogen sulphide (H <sub>2</sub> S).	36 Sulphur dioxide (So <sub>2</sub> ).	59 1:20 55 1:00 (%OO) (%) :81.31 2.46 7.02	7.13 .06 3.65 .06 .06 .06 .06 .06 .06 .06 .06	1.57 .09 4.62 .01 Wethen	42.98 2.59 66.96 .25 7.16 .07 1.48 .08 .86.28 5.18	1.78 .10 7.22 .03 ( <sup>*</sup> N) use south (N) 1.74 27.85 .27 7.48 .22 2.46	Helium (He).	100 6.08 100 .87

¹ In order to see whether the methane came from hydrocarbons soluble in alcohol or ether, this material, after being very finely pulverised, was digested with alcohol (free from organic impurities) for 20 hours; then with fatfree ether for 45 hours. It was then thoroughly washed with ether on a filter which had previously been treated with the same fat-free ether. Afterwards dried at 100° in an oven.

¹ To get rid of all carbonates the powder was treated with concentrated nitric acid for 66 hours. Much gas was given off, including a copious evolution of nitric oxide. The powder was washed until all traces of acid were removed, after which it was dried in an air-bath at 115°. This material heated then gave No. 87.

¹ Treated with dilute sulphuric acid for three days in a vacuum. The powder was washed on a filter until the filtrate was no longer made turbid by barium chloride, and then dried in an oven and heated in an air-bath at 125° for over an hour.

¹ Nos. 92 and 92a. A perfect vacuum was maintained between these two combustions.

¹ Sulphate.

⁰ Carbonated.

¹ The high percentage of nitrogen shown in this analysis is not due to leakage of air, for the pump held its vacuum for days afterwards during the spectroscopic examinations. The yellow helium line, D₂ (λ=5876) stood forth brilliantly, but no argon lines could be seen in the spectrum.

TABLE 8—Continued.

	Specimen No. and remarks,	P. ct. or vol	H <sub>2</sub> S.	SO <sub>2</sub> .	CO <sub>2</sub> .	co.	CH4.	H <sub>2</sub> .	N2.	NH3.	Total.
98.	Quartzite, Rib Hill, near Wausau, Wis. From Samuel Weidman. Famous for its gas bubbles. Powdered on an an- vil and metallic iron thus introduced removed as completely as possible with	P.et. Vol.	0.52	233	68.15	6.87	2.52	19.58	2,41		100
199.	a magnet.  Quartzite, Rib Hill, Wis. Same specimen as No. 98. Granules used instead of fine powder. Crumbles readily into granules, which were treated with boiling hy- drochloric acid to remove any iron	P.ct. Vol.	.17		96.69 .86	.96	.23	1.39	.56 .00	::::	100
100.	which might have come from the anvil. Auriferous, pyritiferous quartz, Cargo, near Orange, New South Wales. No. 837 N. S. W.; No. 3150 U. of W. Dr. Leith. Reduced to a coarse powder on an anvil and treated with boiling dilute hydro- chloric acid which removed any iron in- troduced. After being carefully washed and dried it was more finely reduced in a	P.ct. Vol.	1.07	::::	75.54 .66	3.36	3.99 .04	13.57 .12	2,47	::::	100 .88
101.	porcelain mortar. Beryl from pegmatite dike, New England. Walker Museum Collection. Material for this analysis taken from a massive beryl, 8 inches in diameter, as transpar- ent as window-glass and without visible inclusions or impurities. Instead of be- ing pulverized the material was used in the form of small fragments which were washed with boiling hydrochloric acid. After heating, the transparent frag- ments became white and opaque, resem-	P.ct. Vol.	.34	1111	35.05 .15	3.37	1.37	55.83 .24	4.04	::::	100 .42
101a	bling porcelain.  As 7½ hours failed to expel all the gas, the vacuum was maintained overnight, and the material heated 4 hours more	P.et. Vol.	****	::::	10.0 .01	2.2	5.6	76.9 .07	5.3	::::	100,08
102.	next day.  Pegmatite, containing many crystals of tourmaline, Chesterfield, Mass. Walker	P.ct. Vol.	.04	1001	3.70 .06	3.53 .06	3.03 .05	87.21 1.45	2.42 .04	0.07	100 1.66
103.	Museum.  Quartz from pegmatite vein, Jones Falls, Baltimore, Md. No. 2211, Univ. of Wis. collection. Dr. Leith. Specimen con- tained a large crystal of microcline over 2 inches in length, indicating conditions favorable to crystallization. No micro- cline was used for the analysis, however.  If pegmatites contain much gas, it was thought this one should yield a good	P.et. Vol.	::::	333	68,4	13,9	2.9	7.4	7.4	****	100
104.	volume.  Albite, Gibb's mica mine, Yancey Co., N. C. Walker Museum.	P.ct. Vol.			9.3	11.3 .01	19.6	59.8 .04		::::	100
105.	Quartz from Miocene lava, Iron Co., Utah. No. 46614 U. S. G. S. From E. C. Harder.	P.ct. Vol.	.22	****	57.71 .12	27.12 .05	2.	32 00	12.63 .03		100
106.	Allegan meteorite, a stony aerolite which fell at Allegan. Mich., July 10, 1899, and was dug out of the sand still hot, within 5 minutes of its fall. From U. S. National Museum through G. P. Merrill. Described by Merrill and Stokes (Proc. Washington Academy of Sciences, vol. 2, pp. 41-68). Before extracting the gas, the powdered meteoric material was heated in a vacuum at 150° for 3 hours in the presence of phosphorus pentoxide. Apparatus was then allowed to stand for 20 hours to enable the drying agent to absorb all moisture not	P.ct. Vol.	trace .00	;;;;	41.74 ,21	38.61	2.92	16.73	.00	****	100,49

¹The volume of carbon dioxide being much greater in the case of the granules than in the finely reduced powder strongly suggests that much of this gas is mechanically inclosed in cavities within the quartate, and escapes when the granules are pulverized. This opinion was strengthened by a slight cracking noise which came from within the tube as soon as heat was applied. The gas came off with a rush when the tube was heated. \*No. 6. Chemical analysis by Dr. H. N. Stokes: Metallic part, 2.06 per cent., as follows: Fe, 2.09; Cu, 01; Ni, 1.81; Co, .15. Stony part, 76.94 per cent., as follows: SiO<sub>2</sub>, 34.95; TiO<sub>2</sub>, .06; P.O<sub>3</sub>, .27; Al<sub>2</sub>O<sub>3</sub>, 2.55; Cr<sub>2</sub>O<sub>3</sub>, .53; FeO, 8.47; FeS, 5.05; MnO, .18; CaO, 1.78; MgO, 21.99; K<sub>2</sub>O, .23; Na<sub>2</sub>O, .66; H<sub>2</sub>O at 110<sup>5</sup>, .06; above 110<sup>5</sup>, .19; 100.00.

# TABLE 8-Concluded.

	Specimen No. and remarks,	P. ct. or vol.	H <sub>2</sub> S.	SO <sub>2</sub> .	CO2.	co.	CH4.	Hg.	N <sub>2</sub> .	NH <sub>3</sub> .	Total.
1107.	Estacado meteorite, fell near Estacado, Tex., in 1882. Described by K. S. Howard (Am. Jour. Sci., vol. 22 (1906), pp. 55-60). Kept in a vacuum at ordinary temperature with phosphorus pentoxide for 66 hours; then heated at 150° for 5 hours, and allowed to remain in vacuo for 19 hours more, before attempting to extract the gas.	P.ct. Vol.	0.39		28.47 .24	29.31 .25	3.39	36.25 .31	1.69	::::	100 .84
	Toluca meteorite, a medium octahedrite from Toluca, Mexico.  § First determination  § Third determination  Iron ore, Iron Co., Utah. No.—, U.S. G.S. From C. K. Leith. Chiefly limonite and magnetite, with some iron carbonate	P.et. Vol. P.et. Vol. P.et. Vol.	.02 .00 .10 .01 .13 .00		43.29 10.57 22.82 2.25 6.40 ,12	35.48 8.67 53.99 5.45 71.05 1.32	1.44 ,35 1.91 ,19 2.35 ,04	17.84 4.36 18.49 1.87 14.54 .27	1.93 .47 3.19 .32 5.53 .10	::::	100 24.42 100 10.09 100 1.85
	and sulphate: First portion (gas which came off in 20 minutes).	P.ct. Vol.	****	51.35 11.55	20.62 4.64	27.35 6.15		.68 .15		3111	100 22,49
	Second portion (gas which came off in the next 40 minutes).	P.ct. Vol.	Kana Kitak	48.75 10.65	20.43 4.47	30.12 6.58	.03	.44	.23	::::	100 21.85
	Third portion (material heated 3 hours more).	P.et. Vol.	****	51.40 1.72	14.92 .50	33.28 1.12		.40			100 3.35
110.	Basaltic lava, Kilauea, Hawaii, Cascade of 1868. A rather porous lava, having a specific gravity of only 2.00.	P.ct. Vol.	.88 .01	::::	70,42 .60	21.41 .18	2.49	2.01	2.79	****	100
111.	Fresh lava, Vesuvius, from the lava stream of April, 1906, collected by F. B. Taylor, March 30, 1907. From south side of a quarry in front of the church in Bosco Trecase, above Torre Annunxiata. This specimen came from 10 ft. below the top and 2½ ft. from the bottom of the flow,	P.et. Vol.		.86 .03	78.22 .81	12.24 .05	2.33	1.47	1.88	::::	100
112.	which had been blasted at this point. Fresh lava, Vesuvius, same flow as last; 0.5 kilometer SE. of church where No. 111 was collected. About 8 ft. below surface and 2 ft. from bottom of bed. Collected March 30, 1907, by F. Taylor.	P.et. Vol.		.43	63.49 .39	7,94 ,05	2.33	1.50	1.81	::::	100 .62

1 No. 107. Chemical analysis by J. M. Davison; Fe, 14.68; Ni, 1.60; Co, .08; 8, 1.37; P, .15; SiO<sub>3</sub>, 35.82; FeO, 15.53; MgO, 22.74; CaO, 2.99; Al<sub>2</sub>O<sub>3</sub>, 3.60; Na<sub>2</sub>O, 2.07; K<sub>2</sub>O, .32; 100.95.

3 No. 108. Average of 13 analyses compiled by Farrington (Pub. Field Columbian Museum No. 120, pp. 82-84): Fe, 89.66; Ni, 7.90; Co, 0.63; P, 0.24; S, 0.14; Si, 0.02; Misc., 0.57; 99.16.

4 The material used in this determination consisted of bright borings carefully freed from rust, a pocket of which unfortunately was encountered in drilling. But in spite of much care exercised in drawing out the metallic borings with a magnet, some rust adhered to them and consequently was heated with the metal in the combustion tube. However, this amounted to much less than in the first determination. No filings were used.

5 For this determination borings from the interior of the specimen were carefully made by Wm. Gaertner & Co., scientific-instrument makers. There was no visible rust adhering to these borings, which were them worked twice, with a magnet, without any impurities being left behind. The white paper on which this operation was performed failed to show the slightest discoloration, such as it had done in the two previous determinations. As usual the material was heated at 100° for 3 hours, in the presence of P<sub>2</sub>O<sub>2</sub>, and then allowed to stand in the vacuum overnight to remove all free moisture. Though the vacuum was perfect at the end of this time, the first two pumpings of gas (amounting to 0.2 cubic centimeter) which were evolved when heat was applied, were not kept, since it was desired to eliminate atmospheric air as a source of nitrogen.

A comparison of the three determinations, No. 108 shows what a tremendous effect the presence of a little iron rust will have upon the gases evolved from a metallic meteorite. Much of this gas is doubtless derived from iron carbonate and the hydrated oxide of iron, as will be explained under the topic of gas due to chemical reactions. The most striking feature of these analyses is

#### GROUPINGS AND CLASSIFICATIONS OF ANALYSES.

As the volumes and relative proportions of the gases found in the foregoing analyses vary within wide limits, the nature of this variation can best be shown by grouping the results. To make these tables as complete as possible, not only the results of the present studies, but all the available analyses of other investigators, have been included in the lists. Except in the case of four of the five analyses by Tilden, relative to which sufficient data are not given, all of the figures in these tables refer to volumes of gas per volume of rock. Previous investigators have usually given the total volume of gas and the percentages of each constituent. From these I have calculated the volumes for each individual gas.

TABLE 9.—Analyses classified by groups of rocks.

No.	Rock and locality.	H <sub>2</sub> 8.	CO <sub>2</sub> .	co.	CH <sub>4</sub> .	$\mathbf{H}_2$ .	N2.	Total.	Analyst,
1 2 4 9 19 20 21 22 24 25 26 33 37 38 39 57 66	Granites and gneisses of igneous origin. Granite, Skye (p. ct.). Granite, Vire (average) Granitoid porphyry, L'Esterel Medium-grained, white granite. Coarse-grained, reddish granite. Laurentian gneiss, Ontario. Pike's Peak granite Granite porphyry, Menominee. Fine-grained gneiss, Menominee. Fine-grained banded gneiss, Menominee. Laurentian granite, Marquette. Pink granite, North Carolina Gray granite, Russia. Gray granite, Russia. Laurentian gneiss, Marquette. Oglesby blue granite, Georgia. Stone Mountain granite, Georgia. Ortonville granite, Minn. Granite porphyry bowler, New York. Gneiss of igneous origin, Ontario.		28.60 .86 4.50 .28 .42 .31 .37 3.51 1.89 .6.63 1.89 .1.79 .85 1.13 .08 1.20 carb28	6.45 .35 .32 .07 .08 .06 .72 .23 .113 .05 .09 .18 .15 .11 .03 .05 .11 .03	3.02 .12 .19 .07 .10 .06 .02 .06 .02 .06 .03 .02 .06 .03 .01 .01 .01	61.68 5.29 2.36 .92 2.94 1.50 .04 2.34 3.1.37 .74 .38 1.04 .99 1.79 1.06 .60 .05 .85 .95	5.13 .04 .16 .10 .11 .13 .12 .22 .23 .08 .15 .04 .02  .05 .04 .05 .04	99.88 6.71 7.53 1.44 3.66 2.08 .60 6.85 2.80 9.27 2.94 .65 2.96 2.98 2.38 .76 1.36 1.32 1.32 1.32 1.32	Tilden. Gautier. Do Do Chamberlin Do
	Average of 19 analyses	tr.	1.47	.22	.05	1.36	.09	3.19	
44 51 58 56	The syenite group.  Nephelite syenite, Ontario  Shonkinite, Highwood Mountains, Mont. Quartz syenite porphyry, Colorado  Hornblende syenite, Maine  Average of 4 analyses.	tr. tr.	0.29 .11 carb. .15	0.05 .06 .11 .07	0.04 .05 .08 .03	0.25 .95 .22 2.22	0.05 .05 .03 .03	0.68 1.22 .44 2.50	Chamberlin Do Do Do
15 16 17 32 36 52 58 60 73 74	The gabbro-diorite group.  Gabbro, Lizard, England (p. ct.)		5.50 .00 .40 carb. .44 20.07 .16 1.08 .28 .22 .27 .21	2.16 .00 .10 .12 .58 .07 .07 .06 .07 .04	2.03 .04 .02 .07 .20 .04 .04 .05 .04 .20	88.42 1.40 1.13 .97 2.68 8.54 .52 .93 .45 1.10 1.29 3.95	1.90 .14 .12 .33 .32 .05 .03 .03 .06 .05 .14	100.01 1.40 1.81 1.23 3.64 29.73 .84 2.25 .87 1.52 1.78 4.61	Tilden, Travers, Chamberlin Do Do Do Do Do Do Do Do Do
11 34	Diabases and basalts.  Basalt, Antrim Ophite, Villefranque (average) Lherzolite, Lherz. Keweenawan diabase, Wisconsin Keewatin greenstone, Mesabi.	1.86 1.19	2.57 2.39 12.29 .59 20.08	1.61 .33 .31 .05 1.16	0.80 .08 tr. .19	2.89 4.52 1.15 3.83 10.10	.13 .02 tr. .25 .57	8.00 7.58 15.61 4.91 32.19	Tilden, Gautier. Do Chamberlin

TABLE 9.—Analyses classified by groups of rocks.—Continued.

No.	Rock and locality.	H <sub>2</sub> S,	COg.	00.	CH4.	H <sub>2</sub> .	N <sub>2</sub> .	Total.	Analyst.
35 45 50 61 84 85 110 111 112	Diabases and basalis—Cont. Keweenswan diabase, Minnesota. Iron basalt, Greenland. Nephelite melilite basalt, Texas Diabase, Nahant, Mass. Vogesite, La Plata, Colo. Keweenswan diabase, Michigan. Basalt of 1868, Kilauea, Hawaii. Lava of 1906, Vesuvius.	0.01 tr. .05 .19 tr. .01 .03	0.25 3.74 1.07 4.91 carb. 1.31 .60 .31	0.06 1.74 .20 .21 .14 .09 .18 .05	0.06 .17 .06 .12 .03 .09 .02 .01	3.15 2.24 1.16 3.13 1.08 2.34 .02 .01	0.06 .16 .10 .15 .05 .05 .02 .01	3,59 8,05 2,64 8,71 1,30 3,88 ,85 ,42 ,62	Chamberlin Do
Н	Average of 14 analyses	.19	3.96	.44	.12	2.54	11	7.36	
13 47 62 64 70 72 91	Andesites.  Andesite, Ouray Co., Colo. Andesite, Red Mountain, Ariz. Andesite, Rosita Hills, Colo. Andesite, Lipari Islands Andesite, Granite Mountain, Utah. Phonolite trachyte, Pike's Peak Andesite, summit of Orizaba.	tr. tr. tr.	carb. 5.12 carb. .56 2.66 .76 .22	.09 .57 .27 .04 .16 .05	.02 .30 .05 .01 .03 .03	.08 .12 .30 .17 .53 .19	.08 .26 .13 .02 .05 .06 .03	.27 6.37 .75 .80 3.43 1.08	Chamberlin Do Do Do Do Do Do
	Average of 7 analyses		1.86	.18	.06	.20	.09	2.39	
10 49	Rhyolite, Marble Mountain, Arizona Rhyolite vitrophyre, Teiluride	::::	.22 2.33	.08	.04	.08	.18	.50 2.51	Chamberlin. Do
	Pitchstone rhyolite, Rosita Hills		.07	****	- 14	13		,20	Do
59	Nevadite, Chalk Mountain, Colo  Average of 4 analyses		.15	.05	.01	.02	.03	.27	Do
3 23	Schists. Keewatin schist, Mesabi	****	7.67 .46 4.06	.28	.05	3.81 3.07	.22 .05	12.03 3.72 7.87	Chamberlin Do
	Average	===	4.00	=	=	9,44	-10	==	
14 78	Miscellaneous porphyries.  Coarse porphyry, Ouray Co., Colo  Topaz quartz-porphyry, Saxony	::::	carb.	.05	.02	.22 .44	.01	.80 .97	Chamberlin Do
	Average	****	.32	06	04		.04	.79	
71 83 100 103 105	Quartz.  Smoky quartz, Branchville, Conn.  Vein quartz, Iron Co., Utah  Crystals (aqueous origin), North Carolina.  Auriferous quartz, New South Wales  Quartz from pegmatite, Baltimore  Quartz from lava, Utah  Average of 6 analyses	tr. tr. .01	.07 .11 .03 .66 .09 .12	.00 .09 tr. .03 .02 .05	.00 .03 tr. .04 tr. .00	.00 .53 .01 .12 .01 tr.	tr. .05 .03 .02 .01 .03	.07 .81 .08 .88 .13 .20	Wright. Chamberlin. Do Do Do Do Do
		=		=	=	=	=	=	
27 28 29 30 31	Metamorphosed sedimentaries.  Pyroxene gneiss, Ceylon (p. ct.)	tr30 tr. tr.	77.72 31.62 .13 1.35 .19 .19 .26	8.06 5.36 .10 .22 .07 .08 .09	0.56 .51 .14 .11 .02 .08 .01	12.49 61.93 4.32 4.02 .65 1.90 .37	1.16 0.56 .04 .10 .04 .08 .03	99.99 99.98 4.73 6.10 .97 2.33 .76	Tilden. Do Chamberlin. Do Do Do Do
43	Sillimanite gneiss, Quebec	SO <sub>2</sub> 2.76	2.05	.09	.03	.05	.07	5.05	Do
54 55	Altered Jurassic shale, Colorado	.11	carb.	.07	.02	.45	.04	.68	Do Do
65	Fine-grained gneiss, Ontario	SO <sub>2</sub> 4.15	} .68			05		4.88	Do
67 68	Feather amphibolite, Ontario	tr. tr. 16	carb.	.48 .26 .16	.03 .05 .05	.32 2.01 2.32	.06 .06	.90 2.31 3.22	Do Do Do
69 92	Amphibolite, Chester, Mass		2,23	1.10	.10	2.84	.13	6.40	Do

TABLE 9.—Analyses classified by groups of rocks.—Concluded.

No.	Rock and locality.	H <sub>0</sub> S.	CO2.	00.	CH4.	Н2.	N <sub>2</sub> .	Total.	Analyst.
5 6 18 41 42	Shales.  Kinderhook shale, Burlington, Iowa Portage shale, Ithaca, N. Y. Hamilton shale, Marysville, Pa. Hamilton shale, Nashville, Tenn. Oil shale, Platteville, Wis.	tr. 29.38 3.90	9.28 1.47 .41 20.10 10.43	0.35 .83 .17 4.38 4.82	0.12 .16 .07 20.67	0.22 1.23 1.45 37.03 7.57	0.15 leak .40 1.26	10.12 3.69 2.50 90.89 48.65	Chamberlin. Do Do Do Do Do Do
	Average of first 3 analyses  Sandstones and quartzites.	==	3.75	.45		97		5.43	
8 12 75 76 77 78 80 81 82 97 98	Potsdam sandstone, Baraboo, Wis. Quartzite schist, Baraboo, Wis. Potsdam sandstone, Ablemans, Wis. Same as last, powdered and reheated. Huronian quartzite, Baraboo, Wis. Red Beds, Colorado City St. Peter sandstone, Minnehaha Falls. Same as last, powdered and reheated. Quartzite, Grenville series, Quebec Micaceous quartzite, Uinta Mountains. Quartzite, Rib Hill, Wis.	tr. tr. tr. tr.	.47 .16 .09 .05 .11 carb. .02 .03 .21 .57 .62 .86	.18 .07 .05 .07 .04 .71 tr. .07 .04 .12 .06	.03 .02 .02 .01 .07 .01 .01 .01 .03 .02 tr.	.01 .03 .13 .23 .24 .32 tr. .17 .09 .63 .17	.38 .06 .05 .08 .03 .06 .01 .21 .01 .06 .02 tr.	1.04 .35 .34 .45 .43 1.16 .04 .49 .59 1.42 .90	Chamberlin. Do
	Average of 12 analyses	.02	.29	.11	.02	.17	.08	.69	72

<sup>&</sup>lt;sup>1</sup>The two bituminous shales which derived the bulk of their gas from the distillation and decomposition of organic matter are necessarily omitted from the average.

TABLE 10.—Various minerals.

No.	Mineral and locality.	H <sub>2</sub> 8.	COg.	co.	H <sub>2</sub> ,	CH <sub>4</sub> .	N2.	A + He.	Total.	Analyst.
	Feldspar		1.20	0.01	0.03	0.01	0.02		1.27	Dewar.
	Celestial graphite		6.66		.18	.39	tr.		7.25	Do
	Graphite, Borrodale		.95	.20	.58	.68	.17		2.60	Do
	Chlorite, Zoptan, Moravia		.33	1.33	5.84			5	7.50	Travers.
	Serpentine, Zermatt	****			2.08	,			2.08	Do
	Mica, Westchester, Pa		.42	.2	2				.64	Do
	Tale, Greiner, Tyrol		.19	.1	1				.30	Do
	Feldspar, Peterhead granite		3.08		55	2444	****		3.63	Do
	Malacone		1.55		.03		.02	.17	1.77	Kitchin and Winterson
7	Muscovite, Canada		1.26	.12	.10	.04	.27		1.79	Chamberlin
40	Biotite, Ortonville granite	0.22	12.45	.23	.30	.06	.21		13.47	Do
48	Pyroxene crystals, Red Mountain	.10	.69	.16	.08	.01	.06	****	1.10	Do
63	Anorthosite Quebec	tr.	2.36	.27	.56	.02	.06		3.27	Do
90	Anorthosite, Quebec		2.37	.18	.06	.02	.08		2.71	Do
93	Pitchblende, Beaver Co., Colo	sul.	carb.	.24	.07	.03	.27	.37	.98	Do
94	Carnotite	tr.	2.46	.23	.05	.02	.22	.04	3.02	Do
95	Greenalite rock, Mesabi		.42	.24	5.18	tr.	.15		5.99	Do
96	Grünerite rock, Mesabi	.02	1.14	.26	1.39	.02	.19		3.02	Do
101	Beryl, pegmatite, New England.	tr.	.16	.01	.31	.01	.02		.50	Do
102	Beryl, pegmatite, New England Pegmatite with tourmaline	tr.	.06	.06	1.45	.05	.04		1.66	Do
104	Albite, Yancey Co., N. C		tr.	.01	.04	.02	****	,,,,,	.07	Do
	Average of 21 analyses	.02	1.88	.19	.92	.06	.08	.03	3,18	

It should, perhaps, be stated that in making this and other averages of analyses, in those cases where, on account of excessive carbonation, no figures are given for carbon dioxide, the average amount of this gas calculated from the other analyses is assumed to be present in those rocks marked "carbonated." This addition is added to the average total and makes this figure slightly greater than the average of the column which it foots. The same method has been used for carbon monoxide in the three of Travers's analyses where carbon monoxide and hydrogen are put together.

TABLE 11 .- Stony meteorites.

No.	Meteorite.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH4.	H <sub>2</sub> .	Ng.	Total.	Analyst,
	Guernsey, Ohio Pultusk, Poland Parnallee, India Weston, Conn. Iowa County, Iowa Kold Bokkeveld Dhurmsala, India Pultusk, Poland Mocs Orgueil.  {	SO <sub>2</sub>	1.80 1.06 2.13 2.83 .88 23.49 1.59 2.34 1.25 } 7.40	0.13 .06 .04 .08 .05 .61 .03 .19 .07	0.06 .06 .05 .04  .82 .10 .27 .09 .87	0.95 .52 .36 .46 1.45 .10 .72 .64 .45	0.05 .04 .04 .08 .12 .21 .03 .09 .07	2.99 1.75 2.63 3.49 2.50 25.23 2.51 3.54 1.94 57.87	Wright, Do
106 107	Allegan, Mich Estacado, Texas	tr.	.21	.19	.03	.08	.01	.84	Chamberlin Do
	Average of 12 analyses	4.00	3.77	.24	.20	.50	.09	8.80	

The figures for the Orgueil meteorite which yielded such a remarkable amount of sulphur dioxide make the average for the sulphur gases an abnormal one. The presence of this gas in quantity must mean that the meteorite has suffered much from weathering and oxidation subsequent to its fall. Considerable troilite has passed into iron sulphate which has been decomposed by the heat of the combustion-furnace.

Omitting the sulphur dioxide of this specimen, the average total volume of gas from stony meteorites is reduced to 4.80 times the volume of the meteoritic material.

TABLE 12.—Iron meteorites.

No.	Meteorite.	H <sub>2</sub> S.	CO <sub>2</sub> ,	co.	CH4.	$\mathbf{H}_{2}$	N <sub>2</sub> .	Total.	Analyst.
108	Lenarto Augusta Co., Va. Tazewell Co., Tenn. Shingle Springs, Cal. Cross Timbers, Tex. Dickson County, Tex. Arva, Hungary Cranbourne, Australia Rowton, Shropshire Toluca, Mexico		0.13 .31 .46 .13 .11 .29 5.92 .04 .33 .12	0.00 1.21 1.31 .12 .19 .34 31.91 1.13 .47 1.32	0.16	2.44 1.14 1.35 .67 .99 1.57 8.57 1.63 4.96 .27	0.28 .51 .05 .05 .73 .63 .62	2.85 3.17 3.17 .97 1.29 2.20 47.13 3.59 6.38 1.85	Graham. Mallet. Wright. Do Do Do Do Flight. Do Chamberlin
	Average	****	.78 .21	3.80 .67	.02	2.36 1.67	.30	7.26 2.83	

<sup>1</sup> Flight, Phil. Trans. No. 172 (1882), pp. 898-894 and p. 896.

Methane was determined in only two of these analyses. In these two it averaged 0.10 volume; but in order to make the figures consistent in the table, it was necessary to average these as if the eight other meteorites yielded no marsh-gas, though it is highly probable that this gas was present and has been included in the figures given for hydrogen.

The unusual amount of gas from the Arva specimen recalls the behavior of the Toluca meteorite, which, at the first attempt, produced 24.42 volumes of gas, owing to the presence of a small quantity of iron rust, but whose pure metal evolved only 1.85 volumes. An average, omitting the Arva, is therefore made.

# AVERAGES OF THE GROUPS. Table 13.—Igneous rocks.

Order.	Type of rock.	No. of analy- ses.	H <sub>2</sub> S.	CO <sub>2</sub> .	œ.	CH <sub>4</sub> .	Н2.	N <sub>2</sub> .	Total.
1 2 8 4 5 6 7 8	Basic schists Diabases and basalts Gabbros and diorites Granites and gneisses Andesites Syenites Rhyolites Miscellaneous porphyries	14 11 19 7 4	0.00 .19 .02 .00 .00 .00	4.06 8.96 2.31 1.47 1.86 .18 .69	0.19 .44 .13 .22 .18 .07 .05	0.05 .12 .07 .05 .06 .05 .02	3.44 2.54 2.09 1.36 .20 .91 .06	0.13 .11 .11 .09 .09 .04 .05	7.87 7.36 4.73 3.19 2.39 1.25 .87 .79

The general averages bring out the fact that, while rocks of each group may vary considerably among themselves, each group as a whole fits into a logical place in relation to the other groups. The established order appears to be, most gas from those rocks which contain the greatest proportion of ferromagnesian minerals. Though much influenced by other conditions, such as relative age and nature of the igneous mass, the general deduction may be made that the volume of gas obtained from rocks varies, in a rough way, in proportion to the percentage of ferromagnesian minerals present. Diabases, basalts, and basic schists take first rank in the quantity of gas evolved. Next to them appear diorites and gabbros which are also near the basic end, but formed under different conditions. Andesites are out of their place in this list, as they take precedence over granites in the proportion of ferromagnesian minerals, but these andesites were all either of Tertiary or Recent age, whereas most of the granites came from Pre-Cambrian formations, and, as the next table will show, ancient igneous rocks yield more gas than modern ones. The rhyolites, which combine a scarcity of basic minerals with Tertiary age, foot the list.

It is to be noted that the rank of a type of rock on the basis of an individual gas does not in all cases correspond to its rank for some other gas, or in respect to total volumes. The andesites tested gave more carbon dioxide than either the granites or the syenites, though both of these types greatly surpassed the andesites in the matter of hydrogen. But this involves another factor: in deep-seated rocks, hydrogen and carbon dioxide are of about equal importance; in surface flows, carbon dioxide predominates. Though carbon monoxide and methane are somewhat variable, the minor gases generally increase or decrease with the total volumes.

TABLE 14.—Rocks of sedimentary origin.

Order.	Type of rock.	No. of analy-	Sul- phur gases.	CO <sub>2</sub> .	00.	CH <sub>4</sub> .	Н2.	N <sub>2</sub> .	Total.
1 2 8	Shales (non-bituminous)	13	0.00 .57 .02	3.72 .77 .29	0.45 .22 .11	0.11 .05 .02	0.97 1.52 .17	0.18 .05 .08	5.43 3.18 .69

Among sedimentary rocks, sandstones and quartzites yield less gas than shales, while the metamorphic group, comprising both altered shales and sandstones, together with modified limestones, take an intermediate position, though they surpass shales in hydrogen and the sulphur gases.

TABLE 15 .- Meteorites.

9	order.	Type of meteorite.	No. of analy- ses.	Sul- phur gases.	003.	<b>co</b> .	CH <sub>4</sub> .	H <sub>2</sub> .	Ng.	Total.
	1 2	Stony Without SO <sub>2</sub> of Orgueil Iron Neglecting Arva	10	4.00 .00 .00	3.77 3.77 .78 .21	0.24 .24 8.80 .67	0.20 .20 .02 .02	0.50 .50 2.86 1.67	0.09 .09 .80 .24	8.80 4.80 7.26 2.88

A comparison of the two types of meteorites indicates that carbon dioxide is much more important in the gas from stony specimens than in that from the metallic bodies, but that iron meteorites yield several times as much carbon monoxide and hydrogen as do the stones. Sufficient data are not at hand to permit a comparison of the amount of marsh-gas from these two types; nitrogen, however, appears to come in greater volume from the iron meteorites.

ANALYSES CLASSIFIED BY THE AGE OF THE ROCKS.<sup>1</sup>
TABLE 16.—Igneous rocks.

Order.	Age.	No. of analy- ses.	H <sub>2</sub> 8.	002.	<b>0</b> 0.	CH <sub>4</sub> .	H <sub>2</sub> .	Ng.	Total.
1 2 8 4	Archean Proterosoic Tertiary Recent lavas	18	0.03 .00 .00 .03	7.44 1.85 1.20 .41	0.85 .81 .18 .07	0.07 .07 .05 .01	8.79 2.08 .58 .06	0.21 .16 .07 .02	11.89 4.47 1.98 .60
	Total Pre-Cambrian Grand total	28 51	.02 .01	2.76 2.16	.23 .18	.06 .05	2.12 1.86	.12 .00	5.81 8.86

In addition to those rocks which could be classed either as Archean or Proterozoic, there were others which could only be called Pre-Cambrian; they are included under the head of Total Pre-Cambrian.

The rapid and steady decline in the quantity of every gas, in passing down the columns from the Archean through the Proterozoic and Tertiary to Recent lavas, is very striking. These differences may be due to a combination of causes. The older rocks may yield more gas than the recent, owing to metasomatic changes which have been slowly taking place within the rocks. If this be so, the analyses indicate that this process is progressing at an exceedingly slow rate. Or the early magmas may have been more highly charged with gas, some of which has escaped as they were worked over and over and brought to the surface in later times. Both of these processes have probably been operative.

TABLE 17.—Sedimentary and meta-sedimentary rocks.

Order.	Age of rocks.	No. of analy- ses.	H.S., 80 <sub>2</sub> .	CO <sub>2</sub> .	00.	СН <sub>4</sub> .	H <sub>2</sub> .	Ng.	Total.
1 2 8	Proterozoic	17 10 1	0.45 .00 .00	0.68 1.84 carb.	0.17 .25 .15	0.04 .05 .04	1.82 .41 .45	0.05 .13 .04	2.71 2.28 .68
	Total	28	.27	.98	.20	.04	.96	.08	2.48

<sup>1</sup> In this classification of analyses by the age of the rocks, and in the following one based on granularity, only my own analyses have been used.

Age appears to make less difference in the gas evolved from sedimentary or meta-sedimentary rocks than it does in the case of igneous rocks. All of the Proterozoic specimens were of metamorphic types, while only one of the Paleozoic sediments had been metamorphosed. The Mesozoic representative was a Jurassic shale altered by an intrusive. The unusual amount of sulphur gas in the Proterozoic list is due to two weathered rocks which contained iron sulphate. However, even with these omitted, the hydrogen sulphide is abnormally high in the rocks of this age. One of the Paleozoic shales was so calcareous as to yield 9.28 volumes of carbon dioxide, which accounts for the large quantity of this gas. The two bituminous shales (analyses 41 and 42) are not included in these averages, since their excessive volume of gas from organic sources would so influence the figures as to disguise some of the characteristics of the other rocks.

ANALYSES CLASSIFIED BY THE GRANULARITY OF THE ROCKS.

Table 18.—Igneous rocks.

Order	. Granularity.	No. of analy- ses.	H <sub>2</sub> 8.	00 <sub>2</sub> .	00.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.
1 2 8 4	Fine-grained Medium-grained Coarse grained Various porphyries (mostly Tertiary)	11	0.02 .01 .01	2.75 2.87 .40	0.81 .17 .10	0.06 .05 .04	1.68 1.41 1.20	0.12 .10 .08	4.94 4.11 1.88

From this table it would appear that the fine-grained rocks give off more gas than those of coarser granularity. One of the reasons for this difference probably lies in the fact that metasomatic changes are favored in fine-grained rocks, whose crystals, being smaller, afford more numerous junction-planes between the crystals, through which solutions more readily traverse the rock than in the coarse-grained varieties. Among other changes, hydration and carbonation should alter fine-grained rocks more effectively than coarse-grained ones.

Fineness of grain in igneous rocks usually means that the lava cooled rapidly, and this would hinder the escape of the inclosed gas. But in the process of slow crystallization, such as produces large crystals and coarse texture, much more of the gas would be likely to be crowded out of the growing crystals. However, as a general rule, fine-grained igneous rocks are surface flows, while coarse-texture types were formed at some depth below the surface, and hence a larger proportion of whatever gas was expelled from the rapidly cooling lavas would be more likely to escape altogether than would be the case with the gas which was excluded from growing crystals in deeper horizons, as in bathylithic intrusions, where final escape was difficult. In this problem of granularity, as in the matter of age, the quantities of gas evolved are probably determined by a combination of complex factors rather than by any single cause.

# RESULTS AT DIFFERENT TEMPERATURES.

The different gases are not all expelled from rock material at the same temperature, nor are they evolved at the same rate. In general, hydrogen sulphide and carbon dioxide are not only the first gases to appear, but

they are more rapidly given off than the others. Carbon monoxide follows the dioxide as the temperature is raised, and generally increases in relative importance, as the latter begins to subside, toward the end of the combustion. Hydrogen and marsh-gas are most conspicuous at high temperatures, and hence attain higher percentages in the last half of the gas than in the first portion. Nitrogen appears to be disengaged with much difficulty, requiring considerable time at an elevated temperature. These general facts may be graphically represented by plotting the curves based on the experiments with the Baltimore gneiss. (See fig. 1.)

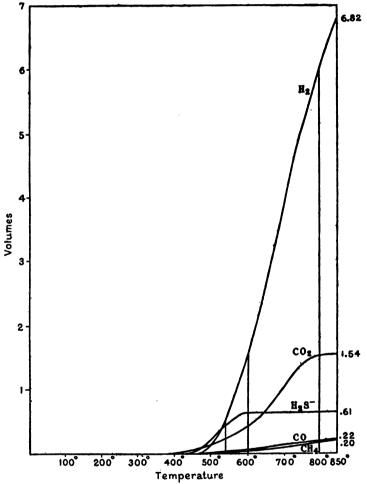


Fig. 1.—Plot of curves representing volume of each gas per volume of rock obtained at different temperatures from Baltimore gneiss.

Nitrogen is omitted from this diagram owing to an unfortunate leakage of air during a part of the experiment, which was sufficient to vitiate the results for this gas.

<sup>&</sup>lt;sup>1</sup> For tables, see pp. 36-37.

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## ABSORPTION.

To determine how much gas might be reabsorbed after being expelled by heat, it was thought desirable to use a rock capable of producing a large volume of gas. For this purpose a diabase from Nahant, Massachusetts. which yielded 13.9 volumes of gas, was selected. This material was heated at full blast until the gas evolution had practically ceased, which required about four hours; 182 cubic centimeters of gas were obtained. After allowing the powder to remain in the vacuum overnight, it was removed and still more finely pulverized in an agate mortar. It was then submitted to forced heat, yielding an additional 20 cubic centimeters of gas in six hours. On the third day the powder gave up but 1 cubic centimeter in four hours. As practically all the gas available under these conditions was now removed, the heat was turned off, and 132.01 cubic centimeters of this gas (at 27.0° and 758 millimeters) immediately introduced into the combustiontube, which was allowed to cool. At the end of 43 hours 101.84 cubic centimeters (at 20.0° and 750 millimeters) remained to be pumped out. This being equivalent to 103.73 cubic centimeters at 27.0° and 758 millimeters, leaves 28.28 cubic centimeters as the volume of gas absorbed by the powder. The material in the tube was now heated for 21 hours, but only 3.47 cubic centimeters could be extracted before the gas evolution ceased. Of this, carbon dioxide constituted more than 85 per cent. There still remain 24.81 cubic centimeters lost in the operation—a loss which is probably to be attributed to the oxidation of that quantity of hydrogen to water by ferric oxide, while the tube was cooling. This water-vapor being removed by the calcium chloride drying-tube, hydrogen could not be again freed by the reverse reaction when the tube was reheated. The carbon dioxide may be explained by carbonation of iron or calcium and the subsequent decomposition of these carbonates when heated the second

In order to ascertain how much absorption there might be at ordinary temperatures, 72 cubic centimeters of the remaining gas, from which the carbon dioxide had been removed, since carbonation is a recognized process, was allowed to stand in the tubes for eight days. At the end of this time no appreciable quantity of the gas had been absorbed. From this and the preceding experiment, it is quite evident that while rock material may take up certain gases while cooling from a higher temperature under special conditions, at ordinary temperatures absorption, if it goes on at all, takes place very slowly. Reversible chemical reactions undoubtedly play an important part in such absorption as takes place under changing temperatures.

Professor Dewar experimented with celestial graphite to ascertain its absorbing power for certain gases. After exhausting the graphite of its gases, dry carbon dioxide was drawn through the tube for twelve hours at ordinary temperatures. The tube was then heated and about 1.1 volumes of gas, containing 98.4 per cent carbon dioxide, pumped off. The graphite on the first heating had given 7.25 volumes of gas, of which 91.8 per cent was carbon dioxide. Dry marsh-gas was next passed over the

powder for twelve hours; upon heating, only 0.9 volume, containing 94.1 per cent carbonic acid, was obtained. The same experiment repeated with hydrogen gave only 0.17 volume, in which carbon dioxide reached 95 per cent.¹ From these figures it would seem that absorption is not very important. The steadily decreasing volumes of gas with each successive heating show the difficulty with which the gas is expelled, for apparently it is liberated more readily after an interval of time than if reheated immediately. Hence, unless the material used be completely deprived of its gas, there is always a danger in assigning to absorption what may, in reality, be only the last portions of the original gas.

Wright used another method in testing the hypothesis that the gas obtained from meteorites has been derived from our atmosphere by a process of absorption. He believed that if the gas be due to absorption from the earth's atmosphere, a meteorite should have stored up more of it after being exposed for a considerable period than shortly after its fall. His original analysis of the gas from a meteorite which fell in Iowa County, Iowa, on February 12, 1875, was made a short time after its fall. A year later, to extract the same quantity of gas from another fragment of the same meteorite required not only a longer time than in the first analysis, but more intense heating as well.<sup>2</sup> If any difference actually existed, a loss rather than a gain was indicated in this interval.

To test the effect of air exposure on a rock powder which had previously been heated until the gas evolution had completely ceased, the exhausted powders of my investigation were kept stored in paper bags, and several of them were reheated after intervals of some months. Two analyses of the iron basalt from Ovifak, Greenland, made 10 months apart, were as follows:

TABLE 19.

	Analysis No. 45.	Analysis after 10 months.
Hydrogen sulphide	0.00	0.00
Carbon dioxide	1.74	1.18 .30
Methane Hydrogen	2.24	.03 .04 .21
Nitrogen	.16 8.05 vols.	

This basalt yielded about one-third as much carbon dioxide after the interval as it did when originally heated, but the hydrogen in the second portion of gas was almost a negligible quantity.

A second test was made with a chloritoid schist from the Black Hills, after an interval of more than a year.

Sir James Dewar, Proc. Roy. Inst., vol. 11 (1886), p. 547.
 Wright, A. W., Am. Jour. Sci., vol. 11 (1876), p. 262.

TABLE 20.

	Analysis No. 23.	Analysis a year later.
Hydrogen sulphide	0.00	0.00
Carbon dioxide	.46 .10	.29 .21
Methane	.04 3.07	.08 2.11
Hydrogen	.05	
Total	3.72 vols.	2.69 vols.

In this case, hydrogen has been restored somewhat more completely than carbon dioxide. Both of them amount to approximately two-thirds of the original volume of these gases.

A third test was made with amphibolite, after an interval of four months.

TABLE 21.

	Analysis No. 94.	Analysis four months later.
Hydrogen sulphide	0.00 2.23	0.00
Carbon monoxide Methane	2.23 1.10 .10	.34 .12
Hydrogen	2.84 .13	1.86 .09
Total	6.40 vols.	

The recovery is here more marked in the case of hydrogen than in that of carbon dioxide.

A fourth test was made with Keweenawan diabase from Houghton, Michigan, after an interval of six months.

TABLE 22.

	Analysis No. 85.	Analysis 6 months later.
Hydrogen sulphide Carbon dioxide	0.00 1.31	0.00 1.33
Carbon monoxide	.09 .09	.08 .03
Hydrogen	2.34 .05	.43 .05
Total	3.88 vols.	1.92 vols.

After reposing six months in a paper bag, this diabase gave as much carbon dioxide, when heated, as it had in the first combustion; but less than one-fifth as much hydrogen was evolved on the second heating.

It is clear that an interval of time partially restores the gas-producing properties of these rock powders. For this phenomenon, there are two possible explanations. Either the first heating does not expel all of the gas contained in the rock, which, by some sort of diffusion or molecular

rearrangement, gradually prepares itself to come off when again heated, or else the rock powder absorbs gases from the atmosphere. If the carbon dioxide were derived from the decomposition, at high temperatures, of a carbonate such as that of calcium, the oxide of calcium thus produced would be likely to capture carbon dioxide from the air, though perhaps this would be a slow process in a paper bag where the circulation of air was comparatively limited. Also, if the hydrogen came from chemical reactions between ferrous salts and water combined in hydrated minerals, the atmosphere might have restored to these minerals some of the water which they lost when first heated. It was thought that rehydration, if combined water be a vital factor in the production of hydrogen, could be more readily effected by placing the exhausted powder in water for a few days than by wrapping it up in a paper bag for as many months.

Accordingly, the Keweenawan diabase powder (No. 85) which originally gave 3.88 volumes, and after six months 1.92 volumes, was heated a third time (a week later) with the evolution of very little gas. This powder, after cooling in the vacuum, was taken out of the combustion-tube and immediately placed in a flask filled with freshly distilled water. A stopper being fitted into the flask, it was allowed to stand for 66 hours. At the end of this time, the water was poured off, the powder quickly, but thoroughly, dried and put into the combustion-tube. When heated, this powder gave off 0.79 volume of gas; but instead of being largely hydrogen, 67.72 per cent of this was carbon dioxide. Hydrogen amounted to only 14.69 per cent, while carbon monoxide reached 15.06 per cent. An analysis of this gas gave:

TABLE 23.

	Percentages.	Volumes.
Carbon dioxide	67.72	0.53
Carbon monoxide	15.06	.12
Methane	.19	.00
Hydrogen	14.69	.12
Nitrogen	2.34	.02
Total	100.00	.79

This carbon dioxide could not have come from the air, but must have existed within the material and must have withstood three successive heatings in the combustion-tube. From a comparison of these figures with the two previous analyses of the gas from this material, what is true of the carbon dioxide would appear to be true of the hydrogen as well. This experiment favors the conclusion, that the gas which is obtained from a rock powder by a second heating after a period of time, is not due to a process of selective absorption from the atmosphere, but rather to changes which have been slowly taking place within the powder itself.

However, the results of these experiments upon the absorption of gas by rock powders at ordinary temperatures and pressures can not throw much light upon the source of the gases, or how they came to be embodied in the rocks, since the conditions under which the rocks were formed must have been very different. While high temperatures, in general, tend to expel the gaseous constituents of the rocks, high pressures would have the effect of promoting absorption. Moreover, it is possible that molten lavas might absorb, or dissolve, certain gases without an increase of pressure. But the testimony of volcanic gases and of the scoriaceous surfaces of lava flows favors the idea that gases and vapors are constantly being boiled out of molten lavas whenever exposed under the ordinary atmospheric pressure. Lavas give off gas rather than absorb it, at the earth's surface; however, at considerable depths below the surface the action may be entirely different. If the conception be entertained that the earth's interior is, for the most part, solid with only threads of liquid lava here and there, the question for this solid portion would be one of the ability of great pressure to cause a solid to absorb gases. This need not be further dwelt upon, since most of the igneous rocks which are accessible have been in the liquid state at some time. In the case of the threads of liquid magma there is reason to suppose that gas, if it could be brought into contact with this lava, would become incorporated in it owing to the great pressure. But this does not explain the original source of the gases, nor how they can be brought in contact with the liquid rock under the prevailing conditions of temperature and pressure.

## STATES IN WHICH THE GASES EXIST IN ROCKS.

In order to explain the immediate source of the gases obtained by heating rock material in vacuo, three different hypotheses naturally present themselves. The simplest of these is to suppose the gases to exist in minute cavities or pores, having been entrapped within the rock during the process of solidification. This supposition is suggested and supported by the observation that microscopic slides of some minerals, notably quartz and topaz, reveal numerous small gas-bubbles. But while there is evidence that some gas is thus held in cavities, there is equally strong evidence to show that the greater part of it can not be attributed to this source.

To escape the difficulties encountered by the first hypothesis, appeal is made to the imperfectly understood property of some of the elements to "occlude," or dissolve within their mass, certain gases. It is remembered that under the proper conditions palladium will occlude 900 times its own volume of hydrogen, and that the same gas is also absorbed, in lesser degree, by other metals, particularly platinum and iron, while silver has a similar affinity for oxygen. This principle applied to igneous rocks as a hypothetical source of their gases becomes at once a more difficult proposition to prove or disprove.

The third hypothesis, more conservative than either of the others, assumes that these gases do not exist in the rocks in the uncombined, or gaseous state, but are produced in the combustion-tube by chemical reactions at high temperature. The oxides of carbon and sulphur are assigned to the decomposition of carbonates and sulphates; methane to organic matter present, carbides, or to high temperature reactions between hydrogen and the carbon gases; sulphureted hydrogen to sulphides; nitrogen to nitrides; while hydrogen is liberated from steam by the action of metallic iron or ferrous salt.

## GASES IN CAVITIES.

The studies of Brewster, Davy, Sorby, Hartley, and others, have established the presence of gas, generally carbon dioxide, though sometimes nitrogen, in the minute cavities of certain crystals. This has been widely known to geologists, and hence, when it was discovered that many crystalline rocks yield gas upon heating in vacuo, it was natural to suppose that the gas came from cavities. Such was the view taken by Tilden. But while microscopical investigations indicated that carbon dioxide constitutes more than 90 per cent of the gaseous matter inclosed in these cavities, and hydrogen is not found in more than traces, the latter gas is the most important constituent of the mixture derived from rocks by heat. In addition to this, the observation that those rocks which are not known to contain many gas cavities produced several times as much gas as the cavernous quartzes also suggested that the bulk of the gas, at least, could not be attributed to inclosure in cavities. Moreover, basic rocks were found to be more productive than acidic, whereas it had generally been supposed that the latter, owing to their greater viscosity, should entrap more gas and vapor than the more fluid basic lavas.

The suspicion that the gas did not come from cavities in any large degree was strengthened by the observation that the composition of the gas varied according to the temperature to which the rock powder was heated. If the gas comes from cavities, its liberation should commence with a slight rise of temperature and should continue more or less steadily, as the heat increases, until the expansive force of the gas opens up most of the pores. Since all gases expand equally, one should burst its confines as soon as another, and a sample of gas obtained at any given temperature should not differ very widely in composition from that evolved at any other.

Neglecting hydrogen sulphide and nitrogen, the character of the gas obtained at various temperatures from Baltimore gneiss 2 is shown by the following table:

TABLE 24.

Gas.	At 860°.	At 448°.	At 540°.	At 600°.	At 800°.	At 850°.
Carbon dioxide Carbon monoxide Methane	6.3 0.0	37.5 4.2 25.0	27.0 2.4 1.8	13.6 2.3 2.5	19.3 2.8 2.1	0.0 1.1 3.4
TotalVolumes	0.0 100.00 .03	33.3 100.00 .03	68.8 100.00 1.28	81.6 100.00 1.40	75.8 100.00 5.30	95.5 100.00 .94

Or, combining the separate analyses so that each figure represents the percentage of the total gas obtained up to the specified temperature, the result is as shown in table 25:

Tilden, Chem. News, vol. 75 (1897), p. 169; Proc. Roy. Soc., vol. 64 (1897), p. 453.
 Material of analysis, No. 28.

TABLE 25.

Gas.	20° to 360°	20° to 448°	20° to 540°	20° to 600°	20° to 800°	20° to 850°
Carbon dioxide	6.3 0.0	69.7 5.3 10.7 14.3	30.1 2.5 2.4 65.0	20.2 2.4 2.5 74.9	19.5 2.7 2.2 75.6	17.5 2.6 2.3 77.6
Total	100.00	100.00	100.00 1.34	100.00 2.74	100.00 8.04	100.00 8.98

Carbon dioxide thus appeared first, constituting 93 per cent of the gas evolved at 360° C., while hydrogen was not present in a measurable quantity. On the other hand, at the highest temperature used (850°) hydrogen amounted to 95 per cent of the total and carbon dioxide was entirely wanting. The steady decrease in the proportion of carbon dioxide with the elevation of the temperature, and the proportionate increase in the value of the hydrogen, are striking. The minor constituents, carbon monoxide and methane, underwent some variations, but did not change so radically. The former came off at the lower temperature, but declined at full red heat. Nitrogen, it appears from other experiments, does not appear in the gases obtained by moderate heating, but increases steadily in importance when the heat is carried higher. It is the last gas to be liberated.

The complete table, expressing the volumes of each gas per unit volume of gneiss, follows:

Table 26.

Temperature.	H₂S.	CO <sub>3</sub> .	<b>co</b> .	CH4.	H <sub>2</sub> .	Total.
100°, boiling water	0.00	0.00	0.00	0.00	0.00	0.00
218°, boiling naphthalene	.00	.00	.00	.00	.00	.00
360°, boiling anthracene	trace	.03	tr.	.00	.00	.03
448°, boiling sulphur		.01	tr.	.01	.01	.03
540°, metal bath		.21	.02	.02	.54	1.28
600°, dull red heat		.17	.03	.03	1.02	1.40
800°, full blast		1.12	.16	.12	4.39	5.30
850°, forced heat		.00	.01	.03	.86	.94
Total	.61	1.54	.22	.20	6.82	8.98

These results are graphically represented in the curves of figure 1.

The fact that little gas could be obtained below 450° is in itself a strong argument against the hypothesis that the gases come from pores, and there also seems no way in which the behavior of the gases, as set forth by these curves, can be consistently fitted into that theory.

## TESTIMONY OF THE METEORITES.

Meteorites have already been subjected to investigation of this sort, though not with this purpose in mind. Mallet divided the gas which he extracted from the meteoric iron of Augusta County, Virginia, into three portions; his results have been reduced by Wright to the figures given in table 27:

<sup>&</sup>lt;sup>1</sup> Mallet, Proc. Roy. Soc., vol. 20, p. 367. 

<sup>2</sup> Wright, Am. Jour. Sci., vol. 2, p. 261.

TABLE 27.

	CO <sub>2</sub> .	∞.	H <sub>2</sub> .	Ng.
Beginning	15.09	30.74	42.5 <b>2</b>	11.65
	4.23	46.12	43.64	6.01
	3.69	47.00	13.36	35.95

The analyses of meteorites by Wright show that, in all cases, carbon dioxide reached a higher percentage in the gas evolved at 500° than it did in that obtained at red heat, and that the reverse of this was true of hydrogen in the stony meteorites. In the iron meteorites, however, two analyses indicated a marked fall in hydrogen with the increase of heat, while the other two were characterized by an increase. Wright's figures for the meteorite from Guernsey County, Ohio, illustrate the continuous decrease in the percentage of carbon dioxide: At 100°, 95.92 p. ct.; at 250°, 86.36 p. ct.; at 500°, 82.28 p. ct.; incipient red heat, 33.55 p. ct.; red heat, 19.16 p. ct.

The volume of gas obtained at each temperature is only stated for 500° and red heat. These show that up to 500°, 2.06 volumes were evolved, and that above this point only 0.93 volume was received. From this it appears that the diminishing percentages of carbon dioxide above 500° represent an absolute slackening of the output of that gas, as well as an apparent decrease due to the greater evolution of hydrogen. It might be argued that in this case, where gas was produced at only 100°, the cavities contributed the carbon dioxide, yielding it early and then slackening, as would be expected; but even if this be admitted, the hydrogen manifestly can not be ascribed to that source. Tending in a measure to support this view is the work of Sorby,¹ who has shown that olivine crystals in the meteorites of Aussun and Parnallee, when examined under the microscope, contain numerous small cavities filled with gas, similar to those which have been observed in many terrestrial minerals.

In his earlier paper, Wright expressed the opinion that the gases were partly condensed upon the particles of iron and partly absorbed within them. Later he took the position that while some gas may be condensed upon the fine particles of iron, a large part of the carbon dioxide, and probably also of the other gases, is mechanically imprisoned in the substance of the meteorite. This view, which does not seem to be in accord with his researches at different temperatures, he bases largely upon a single experiment. Material from the Iowa meteorite was finely pulverized and the iron grains separated from the non-metallic powder. A third portion consisted of coarse fragments of the meteorite. The three portions heated for the same time gave the following results:

TABLE 28.

	CO <sub>2</sub> + CO.	H <sub>2</sub> .	Ng.	Volumes.
Powder Iron Fragments		30.96 59.38 50.93	2.08 1.90 1.00	$\left.\begin{array}{c} 0.97\\0.51\\1.87\end{array}\right\} 1.48$

<sup>&</sup>lt;sup>1</sup> Sorby, Proc. Roy. Soc., vol. 13 (1864), pp. 333-334.

The greater volume of gas from the fragments was taken to indicate that a portion of the gas was lost in the process of pulverization. An analysis of these figures reveals the fact that the difference in volume was chiefly due to the deficiency of the combined portions in hydrogen, instead of carbon dioxide, and that while there was also a slight loss of the latter gas, there was a decided gain in nitrogen.

Returning to the rocks, Tilden is authority for the statement that it does not make much difference in the quantity of gas evolved, whether the material be taken in chunks or in a fine powder. Instead of abandoning the idea of cavities, he believed them to be very minute. But this is approaching an alternative hypothesis; if the reduction of the cavities is carried far enough—to intermolecular spaces—practical occlusion is the result.

Another objection to the theory of mechanically-retained gases apparently exists in the slowness with which the gas is liberated when the material is heated. Usually about three hours and often a very much longer time is required to expel the gas. Unless the gas from cavities be assumed to escape by diffusion through the walls of the inclosing mineral, instead of violently bursting its confines, there is no reason why it should not come off with a rush when the combustion-tube is heated rapidly to redness. Some rocks, generally those yielding a moderate quantity of gas in which carbon dioxide is the principal constituent, often give up their gas quickly mostly within the first 60 to 90 minutes, although the generation continues for a longer time, before ceasing But other varieties of rock, particularly altogether. those noted for greater volumes, in which the percentage of hydrogen runs high, emit gas slowly and steadily for three or four hours.

These considerations led me to try a series of experiments which should show how much gas actually could be obtained from the opening of cavities alone. For this purpose a crusher was devised (fig. 2), capable of pulverizing a rock specimen in a complete vacuum. Adopting the principle of the familiar steel mortar, this was constructed in three pieces. The cylindrical cup in

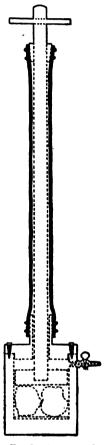


Fig. 2.—Apparatus for crushing rock specimens in vacuo.

which the rock material is crushed possesses an internal diameter of 7 centimeters and a depth of 9 centimeters. The walls are purposely made thick and strong and the bottom is protected from the abrasion of hard minerals by inserting a disk of hardened steel. Inserted in the walls is a stopcock through which the apparatus is to be exhausted and the gases later pumped out. A circular steel cap, or cover, provided with six screws, whose sockets are depressed in the top of the cylinder, is intended to make the chamber of the mortar air-tight. In the center of the cap-

<sup>&</sup>lt;sup>1</sup> Tilden, Chem. News, vol. 75 (1897), p. 169; Proc. Roy. Soc., vol. 64 (1897), p. 453.

piece is a hole large enough to permit the ready movement of the piston-shaft. Around this hole on the upper side there is welded a short piece of steel tubing which is to guide the piston-rod and serve as a place of attachment for the rubber tubing in which the shaft of the piston is incased. The piston is a shaft 50 centimeters in length, 2.2 centimeters in thickness, to which is attached a head piece of hardened steel which will fit snugly into the cylinder. Near the upper end of the piston is a cross-bar serving as a handle, and also a flange to which the rubber tube is to be fitted.

When ready to put together, the piston-shaft is incased in a 1-inch tube of pure rubber, 45 centimeters long, which is tightly fitted and wired to the flange near the end of the rod, whereupon the other end of the shaft is slipped through the hole in the cover-piece, and the piston-head affixed. The lower end of the rubber tube is wired to the steel tube of the cover-piece which, after the rock specimen has been placed in the cylinder, is fitted with a rubber washer and screwed as tightly as possible to the cylinder. The rubber tube is taken of length sufficient to allow the head of the piston to touch the bottom of the cylinder; by pulling upward on the handle the rubber wrinkles and folds upon itself, affording ample play to the piston.

The stopcock is connected with the mercury-pump and the cylinder of the crusher exhausted, after which vigorous strokes delivered at the end of the piston with a heavy mallet crush the rock, thus opening the gas cavities. Whatever gas is liberated, is pumped into the receiver and analyzed in the ordinary way.

#### RESULTS.

Of the first rock tested, a basalt from the Faroë Islands, 42 grams were crushed finely enough to pass through a 30-mesh sieve, besides several times as much, less completely pulverized. In all, less than 0.1 cubic centimeter of gas was obtained, which may be considered as practically no gas at all, since this small quantity is within the leaking possibilities of the apparatus.

A slightly scoriaceous basalt from Hawaii produced about 0.1 cubic centimeter of gas, which appeared to be largely air. No carbon dioxide could be detected. Of this basalt, 18.3 grams passed through the sieve.

15.73 grams of vein quartz from Utah (No. 71 of the analyses) gave no trace of gas.

In an effort to demonstrate conclusively that the lack of gas liberated by crushing these lavas was not due to defective apparatus, a glass bulb of measured capacity, filled with air, was broken in the crusher in place of the rock ordinarily used. The result showed that gas introduced into the crusher can be extracted without sensible change in volume. As diffusion through the rubber tubing was considered a possible, though not very probable, source of error, a further trial was made, using hydrogen, lightest and most active among the gases, in order to put the apparatus to as severe a test as possible. The purity of this hydrogen had previously been established by analysis. The bulb broken, the gas was pumped off and exploded with air. The observed shrinkage agreed, within the limit of error, with the amount of hydrogen calculated to have been contained within the bulb.

Being desirous of finding some specimen which would yield gas when crushed in this manner, I procured some crystals of cavernous quartz from Porretta, Italy, in which several of the cavities exceeded a millimeter in diameter. 5.91 grams were crushed to sufficient fineness to pass through the sieve, and 61.66 grams were partially crushed. 0.08 cubic centimeter of carbon dioxide was obtained, which, supposing that it all came from the 5.91 grams, would be equivalent to only 0.03 of the volume of the quartz. An analysis showed also a little methane and some nitrogen, but the amount of gas available was too small for the determination to be of any value.

The result of this last test agrees with the microscopic studies of the early investigators. Carbon dioxide exists in the cavities of quartz, but its volume, compared with the volume of the inclosing mineral, is small. Microscopical observations seem to show that gas cavities occur almost exclusively in a certain set of minerals which combine hardness usually with imperfect cleavage, namely, quartz, topaz, garnet, spinel, beryl, chrysoberyl, corundum in the form of rubies, sapphires, and emeralds, and diamond. These are minerals which, once they had inclosed gas, would hold it, even under great pressure.

## GASES DUE TO CHEMICAL REACTIONS.

#### HYDROGEN.

The double series of iron salts, ferrous and ferric, together with the intermediate ferroso-ferric compounds, reacting with oxidizing or reducing agents, undergo various reversible reactions whose possibilities are great. When steam is passed over metallic iron or ferrous oxide at a red heat, it is decomposed, giving up oxygen to the iron, and at the same time producing free hydrogen. The reactions may be written:

$$Fe + H_2O = FeO + H_2$$
  $3FeO + H_2O = Fe_3O_4 + H_2$ 

Hydrogen is produced in this way most rapidly at temperatures about 500°. Stromeyer is authority for the statement that the breaking up of water begins at 150° but takes place very slowly; at 200° somewhat more rapidly; at 360° the process requires several hours; at 860° it is complete in less than one hour; while near the melting-point of iron several minutes are sufficient.<sup>1</sup>

The authorities agree that ferric oxide is not formed in this process; the magnetic oxide, Fe<sub>3</sub>O<sub>4</sub> is the final product of the action of a current of steam upon ferrous oxide.<sup>2</sup>

But these reactions are completely reversible. According to Gay-Lussac, magnetite is reduced to the metal by hydrogen at every temperature between 400° and the highest degree of heat obtainable in the combustion-furnace, particularly at the same temperature at which steam is split up by glowing iron.<sup>3</sup> Siewert states that ferric oxide (from the oxalate) is not altered by hydrogen at 270° to 280°; between 280° and 300°

Stromeyer, Pogg. Ann., vol. 9, p. 475.
 Among others, Regnault, Ann. de Chim. et Phys., vol. 62, p. 346.
 Gay-Lussac, Ann. de Chim. et Phys., vol. 1, p. 33.

it is reduced to ferrous oxide, and when heated above 300°, to the metal.¹ The more recent studies of Moissan give different figures;²  $Fe_2O_3$  is reduced by hydrogen at 300° to  $Fe_3O_4$  in 30 minutes; at 500° to FeO in 20 minutes; at 600° to 700° to metallic iron.

If the hydrogen or water-vapor produced by these reactions is not removed, the process continues only until a condition of equilibrium is established. In extracting the gases from rocks, the products of these reactions were rapidly removed, so that final equilibrium was probably never attained. Hence, in these experiments the direction in which the reaction will proceed depends upon whether there is ferrous oxide and water, or ferric oxide and hydrogen, most abundantly stored in the rock. Ferrous and ferric salts behave, in general, like the oxides.

Since most igneous rocks contain ferrous as well as ferric salts, the possibility that, when heated in the presence of steam, hydrogen will be produced, must always be taken into account. In terrestrial rocks water of constitution is generally present and often is not expelled below a bright red heat. Thus, a rock containing a ferrous compound in appreciable amount, together with water of crystallization, a portion of which is retained up to red heat, will be in a condition to furnish hydrogen upon the application of heat.

In general, the analyses show that the greater the amount of iron present in the rock, the more hydrogen may be expected. This may be the result of chemical action, or a selective occlusion of hydrogen manifested by iron and its compounds. Magnetite, being the end product of the reaction of water upon iron, can not produce hydrogen by this chemical interaction, though it might possess the occlusive properties of iron compounds. Analysis of the black sand from the bed of the Snake River, Idaho, indicates that iron in the form of magnetite does not yield much hydrogen. However, these figures have no great significance, for, even though an abundance of hydrogen existed in the ore, either occluded or mechanically imprisoned, the magnetite would, at red heat, quickly oxidize it to water, with the exception of a small portion of free hydrogen maintained by the reverse reaction. The analyses show that basic diabases and basalts yield the most gas, while acidic rhyolites give but little. These are also among the maximum and minimum iron-bearing lavas. But the difference in hydrogen is much greater proportionately than the difference in ferrous salts. Table 13 also shows that andesites, which are nearer the basic end of the scale than the acidic, do not greatly exceed the rhyolites in hydrogen. The difference between the two types of rocks, acidic and basic, in point of volume of the individual gases, while somewhat more conspicuous in the case of hydrogen, is generally true of the other gases as well.

Endeavoring to prove that the hydrogen obtained by heating minerals came entirely from chemical reactions, Travers experimented with the secondary mineral chlorite, calculating how much ferrous iron should have been oxidized to give the quantity of hydrogen and carbon monoxide evolved.<sup>5</sup> This he found to agree closely with the difference in amount of

Siewert, Jahresbericht d. Chem., 1864, p. 265.
 Moissan, Comptes Rendus, vol. 84, p. 1296.
 Analysis No. 46.
 Ante, p. 27.
 Travers, Proc. Roy. Soc., vol. 64, p. 132.

ferrous iron present before and after heating. Another test with feldspar from the Peterhead granite not showing correspondence, seemed to Travers to be explained by the presence of both metallic iron and ferrous oxide in the feldspar. The presence of a considerable amount of metallic iron in a feldspar which crystallized from an acidic magma containing an excess of silica is quite unusual. This feldspar treated with dilute sulphuric acid yielded about four volumes of hydrogen.

Against the theory that the hydrogen was largely derived from the action of water-vapor on ferrous compounds, may be placed the very marked change in color which the rock undergoes during the process of heating. I have observed that whenever a rock powder, before being placed in the tube, possesses an orange, brownish, or reddish tint due to ferric oxide, the combustion invariably alters the tone to a greenish gray. This suggests a reduction of ferric oxide to ferrous oxide, a process consuming hydrogen. In order to test this question, a specimen of bright-red Permian sandstone from the Garden of the Gods near Colorado Springs 1 was powdered. These Red Beds are supposed to consist of thoroughly oxidized material; this opinion was partially confirmed by chemical tests which gave a weak reaction for ferrous iron, but indicated much ferric. After heating, the brick-red sand had become dull gray-green in color. The gray sand from the combustion-tube gave a stronger reaction for ferrous iron. Later, a quantitative determination of the ferrous iron present before and after heating was undertaken. Equal weights of the two sands were boiled with strong sulphuric acid 2 for two hours and then allowed to stand overnight. In each case the solution was effected in an atmosphere of carbon dioxide to prevent oxidation by oxygen from the air. The two solutions were then titrated with potassium permanganate solution. 3.09 grams red sand required 1.97 cubic centimeters N/10 KMnO4; 3.09 grams gray sand required 2.52 cubic centimeters N/10 KMnO4. 0.55 cubic centimeter N/10 KMnO<sub>4</sub> is equivalent to 0.015 gram of iron, which is the weight of the metal reduced from the ferric to the ferrous state. For the total weight of sand used in the gas analysis (85 grams), the increase in ferrous iron should be 0.423 gram, which would correspond to an oxidation of approximately 85 cubic centimeters of hydrogen. Yet both hydrogen and carbon monoxide were obtained from this sandstone in considerable quantities.

TABLE 29.

	Per cent.	Volumes.
Hydrogen sulphide Carbon dioxide	0.05	0.00
Carbon monoxide Methane	60.69	.71 .07
Hydrogen	27.28	.32 .06
Total		1.16

Analysis No. 78

<sup>&</sup>lt;sup>2</sup>3 parts conc. acid to 1 part water.

In order to ascertain the quantitative effect of the presence of ferric oxide in moderate amount, 0.77 gram of pure Fe<sub>2</sub>O<sub>3</sub> was mixed with 20.04 grams of diabase powder, tinting this latter a reddish brown. An analysis of the resulting gas and of the original diabase gave the figures shown in the following table:

TABLE 30.

	Result	ing gas.		Original	diabase.1
	Per cent.	Volumes.		Per cent.	Volumes.
Hydrogen sulphide Carbon dioxide Carbon monoxide Methane Hydrogen	3.90 .87	0.00 7.08 .38 .09 2.01	Hydrogen sulphide Carbon dioxide Carbon monoxide Methane Hydrogen	2.47 1.32	0.00 8.51 .34 .18 4.68
Nitrogen	1.39	.13	Nitrogen		.17
Total	100.00	9.69	Total	100.00	13.88

Analysis No. 86.

A comparison of these results shows that, while the yield of hydrogen was diminished by the ferric oxide to less than half of what it would have been, the carbon monoxide was not affected. The ferric oxide apparently only went down to a state of equilibrium, and was not in sufficient quantity to offset the copious evolution of hydrogen from the diabase. The brown color, however, was replaced by green.

To get rid of the iron, and particularly ferrous iron, material from the same diabase specimen was treated with concentrated nitric acid for 66 hours. Much gas came off at first, nitric oxide, perhaps from the action of the acid on pyrite, being very conspicuous. The powder, washed repeatedly on a filter until all the acid had been removed, was dried in an oven overnight and then heated at 115° in an air-bath for half an hour. Two and a half hours at red heat, in vacuo, then expelled only 0.23 volume of gas from the diabase powder. Its composition is given in table 31.

TABLE 31.

	Per cent.	Volumes.
Hydrogen sulphide Carbon dioxide	0.00	0.00
Carbon dioxide	25.23	.06
Carbon monoxide	20.15	.05
Methane	6.36	.01
Hydrogen	21.21	.05
Hydrogen	27.05	.06
Total	100.00	.23

A similar test was made with dilute sulphuric acid, in a vacuum. In this experiment, the gas driven off by the acid during the first 2½ hours was collected and analyzed. Table 32 shows this to have been chiefly carbon dioxide.

TABLE 32.

	Per cent.	Volumes.
Hydrogen sulphide	0.00	0.00
Carbon dioxide	98.10	6.44
Carbon monoxide }	.03	.00
Hydrogen	.25	.02
Hydrogen	1.62	.10
Total	100.00	6.56

As a precautionary measure, to avoid the introduction of any metallic iron in the process of pulverization, the diabase was reduced to a powder in an agate mortar. The brass sieve was not used. Hence this hydrogen did not come from any action of the acid upon a metal introduced during the manipulations.

This powder, after remaining in a vacuum with an excess of sulphuric acid for three days, was washed thoroughly on a Gooch filter until the last traces of calcium sulphate had been removed. After drying for an hour at 125°, the powder was placed in the combustion-tube and heated to redness. The sulphuric acid left more gas in the rock than the nitric.

TABLE 33.

	Per cent.	Volumes.
Hydrogen sulphide	13.30	0.21
Hydrogen sulphide  Carbon dioxide	38.19	.62
Carbon monoxide	9.01	.14
Methane	3.95	.06
Hydrogen	33.80	.54
Hydrogen	1.75	.03
Total	100.00	1.60

From these experiments it would appear that acids remove the critical gas-producing factors without liberating a notable amount of any gas except carbon dioxide. Whether hydrogen may not pass into solution with the iron, without being freed, is a question which naturally arises, but the balance of chemical opinion is against this supposition.

Professor Dewar digested celestial graphite in strong nitric acid for several hours and, after washing and drying, found that with heat it gave exactly the same amount of hydrogen as before treating with the acid. This would suggest that, in the case of celestial graphite, the hydrogen was not connected with iron, but existed in some very stable form.

If all the hydrogen was produced by the reaction of water on ferrous salts, it would seem as if the volume obtained should bear a direct relation to the quantity of these two critical constituents present in the rock. To throw light on this matter, two rocks of the same origin, but of different chemical composition, presented the most favorable line of attack. An intrusive andesite and a specimen of vein quartz derived from the mag-

<sup>&</sup>lt;sup>1</sup> Dewar, Proc. Roy. Inst., vol. 11, p. 550.

matic waters of the intrusion, kindly furnished by Dr. C. K. Leith, were used to illustrate this point. Though containing very different quantities of ferrous compounds, they yielded identical volumes of methane, hydrogen, and nitrogen. These analyses are given in table 34.

TABLE 34.

And	esite.		Vein	quarts.
Per cent.	Volumes.		Per cent.	Volumes.
0.03	0.00	Hydrogen sulphide	0.00	0.00
4.75	.16	Carbon monoxide	11.26	.11 .09
15.35	.53	Hydrogen	64.40	.03 .53
		, i		.05
	0.03 77.50 4.75 .95 15.35 1.42	4.75 .16 .95 .03 15.35 .53 1.42 .05	Per cent. Volumes.    0.03   0.00   Hydrogen sulphide       77.50   2.66   Carbon dioxide       4.75   .16   Carbon monoxide       95   .03   Methane       15.35   .53   Hydrogen       1.42   .05   Nitrogen	Per cent.         Volumes.         Per cent.           0.03         0.00         Hydrogen sulphide         0.00           77.50         2.66         Carbon dioxide         13.93           4.75         .16         Carbon monoxide         11.26           .95         .03         Methane         4.00           15.35         .53         Hydrogen         64.40           1.42         .05         Nitrogen         6.41

The great excess of carbon dioxide in the andesite is assigned to carbonation of that lava subsequent to its formation—a process to which the quartz would not be susceptible.

The observation that comparatively pure quartz yielded half a volume of hydrogen suggested a quantitative analysis to determine the amount of iron actually contained in hydrogen-producing quartz. For the purpose quartz from Orange, New South Wales, was selected. 102.72 grams of the quartz yielded 4.81 cubic centimeters of hydrogen at 0° and 760 millimeters.<sup>2</sup> After the gas had been extracted, two different portions of the exhausted mineral were digested with aqua regia—one of them boiled for an hour, the other being allowed to stand during several days, and occasionally warmed to the boiling-point. The acid may be considered to have dissolved all the iron from which gas could have escaped. To make the case certain, all of the iron detected has been supposed to have existed in the quartz as ferrous oxide, although some of it undoubtedly occurred in the form of ferric compounds. The iron was weighed as Fe<sub>2</sub>O<sub>3</sub>.

## First determination:

22.22 gms. quartz contained	.00485 gm. Fe .00748 gm. .65 c.c. 4.81 c.c.
Second determination:	
52.02 gms. quartz contained.  102.72 gms. quartz would contain.  102.72 gms. quartz would contain.  Fe (as FeO) required to give 1 c.c. hydrogen.  Maximum amount hydrogen from reaction.  Amount of hydrogen actually obtained.  Hydrogen not from this reaction.	.00829 gm. Fe <sub>3</sub> O <sub>3</sub> .00580 gm. Fe .00748 gm. .77 c.c. 4.81 c.c.

<sup>&</sup>lt;sup>1</sup> Analyses Nos. 70 and 71. <sup>2</sup> Analysis No. 100.

According to these two determinations, this quartz evolved respectively 7.4 or 6.2 times as much hydrogen as could have been generated by the reaction  $3\text{FeO} + \text{H}_2\text{O} = \text{Fe}_2\text{O}_4 + \text{H}_2$ .

If the iron existed as pyrite, four times as much hydrogen as could come from ferrous oxide might have been produced in accordance with the equation

 $3\text{FeS}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2 + 6\text{S}$ 

On the basis of this equation the excess of hydrogen from the quartz is much reduced.

## First determination:

102.72 gms. quartz contain	0.00485 gm. Fe
Fe (se FeS.) required to give 1 c c hydrogen	00187 em
Hydrogen possible from reaction	2.60 c.c.
Hydrogen possible from reaction.  Hydrogen actually obtained.	4.81 c.c.
Hydrogen not from this reaction	2.21 c.c.

#### Second determination:

102.72 gms. quarts contain	0.00580 gm. Fe
Fe (as FeS.) required to give 1 c.c. hydrogen	.00187 gm.
Hydrogen possible from reaction	3 08 c c
Hydrogen actually obtained	4.81 c.c.
Hydrogen not from this reaction	1.73 c.c.

These computations assume not only that all the iron in the quartz was combined as pyrite, and that it was completely oxidized to magnetite, but that the hydrogen sulphide produced was entirely dissociated into hydrogen and sulphur. But the iodine titration in the gas analysis revealed 0.36 cubic centimeter (at 0° and 760 millimeters) of sulphur gas whose odor was that of hydrogen sulphide rather than sulphur dioxide. If this were H<sub>2</sub>S, it would diminish the amount of hydrogen which could have come from the reaction by 0.36 cubic centimeter; if, however, it were sulphur dioxide the volume of possible hydrogen would be swelled by 0.72 cubic centimeter in accordance with the reaction

$$S + 2H_2O = SO_2 + 2H_2$$

But as there was certainly much more hydrogen sulphide than sulphur dioxide absorbed by the potassium hydroxide solution, it will be safe to balance the possible SO<sub>2</sub> formed, by the H<sub>2</sub>S undissociated, and ignore these corrections, which would probably reduce, rather than increase, the quantity of hydrogen which might result from pyrite.

If the iron had all been locked up in the mineral chalcopyrite (CuFeS<sub>2</sub>) the hydrogen might be accounted for, but chemical tests failed to detect the copper which this supposition would require. Just how much hydrogen might be expected from iron nitride (Fe<sub>2</sub>N) is not certain, since, in the presence of superheated steam, the nitrogen is more likely to unite with hydrogen and come off as ammonia rather than as free nitrogen, and ammonia is not dissociated short of the electric spark. That most of the iron in the quartz is in the form of a nitride is highly improbable. Iron carbide also would not yield sufficient hydrogen.

Another mineral apparently containing very little iron, but which yielded considerable hydrogen, was the beryl of analyses 101 and 101a.

Though as transparent as window-glass, one volume of this beryl contributed 0.31 volume of hydrogen. A determination of its accessible iron was made by pursuing the same method as was used for the quartz. The results were:

35.00 gms. beryl contained	0.0003 gm. Fe <sub>2</sub> O <sub>2</sub>
127.52 gms. beryl would contain	.00109 gm. Fe <sub>2</sub> O <sub>2</sub>
127.52 gms. beryl would contain	.00076 gm. Fe
Fe (as FeO) required to give 1 c.c. hydrogen	.00748 gm.
Maximum amount hydrogen from reaction	0.10 c.c.
Hydrogen actually obtained (0° and 760 mm.)	l4.89 c.c.
Hydrogen not from this reaction	l4.79 c.c.

This beryl expelled nearly 150 times as much hydrogen as can be assigned to the interaction of steam and ferrous oxide under the most generous assumptions. The actual hydrogen is 37 times the maximum quantity possible from this weight of iron, either as pyrite or in the metallic state. Here is a very declared case demonstrating the inadequacy of chemical reactions involving iron to generate the hydrogen obtained.

Heated in a closed tube with a limited amount of air, beryl is known to give up a small quantity of water which, in some varieties of the mineral, may reach 2 per cent. The question whether the excess of hydrogen over that possible from reactions between water and iron could have arisen from the dissociation of this water is easily answered. The recent researches of Nernst upon the dissociation of steam indicate that, at temperatures below 2000° C., the process takes place only to a very limited extent. At 1124° C., which is somewhat above the point to which the beryl was heated, only 0.0078 per cent of the total steam can be dissociated.1 At this temperature, 127 grams of beryl containing 2 per cent of water should, on the basis of Nernst's figures, yield 0.24 cubic centimeter of hydrogen, provided the gas was quickly cooled. Hence only a small portion of the hydrogen can be attributed to the dissociation of water present in the mineral.

To the question of the importance of ferrous salts in the production of hydrogen, it is possible that meteorites, which have usually been regarded as free from water, can add testimony of some value. Though it is true that in freshly fallen specimens hydrous minerals have not yet been recognized,2 nevertheless, the researches of Graham, Mallet, Wright, and Dewar, besides my analyses of the Allegan, Estacado, and Toluca meteorites, have shown that these bodies, when heated, give off much gas, rich in hydrogen. If these meteorites really contained no water, either original or by absorption from the earth's atmosphere, the hydrogen obtained from them can not be attributed to the decomposition of water; it must have been held within the mass of each meteorite, either entrapped or occluded.3 But in several instances, at least, the investigators have stated that a certain quantity of water was driven off, though perhaps this came from weathered aerolites. The chemical analysis of the Allegan meteorite,

Nernst, Chem. Central-Blatt, 1905, 2, p. 290.
 Farrington, Jour. of Geol., vol. 9 (1901), p. 532.
 It is to be remembered that a few meteorites have been found to contain hydrocarbons, from which hydrogen might arise, but the presence of these hydrocarbons from inorganic sources is more remarkable than that of hydrogen itself.

which was dug up while still hot, gave Stokes 0.25 per cent of water.1 Perhaps this was moisture absorbed from the air by deliquescent compounds, such as lawrencite; still, on the other hand, there appears no reason, at the present time, why a part of this water should not be a primary constituent of the meteorite. This uncertainty points out the desirability of further, and more critical, studies upon the composition and properties of meteorites, before attempting to base an argument upon the absence of water in these bodies.

Other possible sources of hydrogen are hydrogen sulphide, hydrocarbons, and the products of radioactivity. As the decomposition of sulphureted hydrogen has already been mentioned, and is also treated under the head of that gas, it need not be discussed here. Hydrocarbons can only be represented in small quantities in igneous rocks, and should produce more methane than free hydrogen. Unless the analysis shows much marsh-gas, hydrogen from this source must be unimportant.

#### CARBON DIOXIDE.

The carbonates of most metals are decomposed by heat with the liberation of carbon dioxide. On this account the determination of the carbon dioxide yielded by rocks which have undergone much carbonation is of little value. Many rocks which appear to be perfectly fresh have nevertheless suffered slight carbonation while in the zone of weathering, and thus possess carbon dioxide in a combined state ready to be evolved when sufficiently heated. This carbon dioxide from the non-gaseous constituents of the rock embarrasses the determination of the free gas, since there is no way of separating the carbonic acid from these different sources.

The degree of heat necessary to decompose carbonates throws some Erdmann and Marchand state that already at light on the question. 400° traces of carbon dioxide are given off from calcium carbonate.2 The studies of Debray show that at the boiling-points of mercury and sulphur, 350° and 448° respectively, the development of CO<sub>2</sub> from calcite in vacuo is inappreciable. The same investigator found that at 860° calcite gives up carbonic anhydride until a pressure of 85 millimeters is reached, when the action ceases. At 1040° the pressure may rise to 520 millimeters before the evolution of gas is stopped. In the presence of carbon dioxide at the ordinary atmospheric pressure, calcite retains all of its optical and other properties unaltered, even at 1040°. Carbon dioxide from calcium carbonate is thus not of any quantitative importance below 450°. In general, most of the carbonic acid from the rocks is expelled at temperatures above 450°. But considerable CO<sub>2</sub> often appears before the heat reaches 400°, as is shown by the Baltimore gneiss. Perhaps this gas may be assigned to ferrous carbonate. Iron carbonate would be expected to decompose more readily than calcium carbonate, though I have been unable to discover at what temperature the process commences.

<sup>&</sup>lt;sup>1</sup> Ante, p. 21. <sup>2</sup> Erdmann and Marchand, cited by Gmelin-Kraut, Anorg. Chem., 2, p. 354. <sup>3</sup> Debray, Comptes Rendus, vol. 64, p. 603.

When a finely powdered igneous rock is treated with hydrochloric acid and gently warmed, a few small bubbles of carbon dioxide usually are seen to rise to the surface of the acid. This gas comes from the action of the acid upon small quantities of carbonate present in the rock. To test the quantitative importance of this action and to discover whether other gases are freed by acid, 25.13 grams of diabase from Nahant, Massachusetts, were placed in a flask connected with the mercury-pump, and the air removed. Dilute sulphuric acid was introduced into the flask through a dropping funnel. The gas developed in the cold during the first 2½ hours was found to have the following composition:

TABLE 35.

	Per cent.	Volumes.
Hydrogen sulphide	0.00	
Hydrogen sulphide Carbon dioxide	98.10	6.44
Methane	.03	.00
Hydrogen	.25	.02
Nitrogen	1.62	.10
Total	100.00	6.56

Practically all of the carbon dioxide thus set free is to be assigned to a carbonate.

The apparatus was allowed to stand for three days, during which time more gas came off. At the end of this period, the powder was washed, dried, and then submitted to the ordinary process of heating in the tube. Of the gas received, 38.19 per cent, or 0.62 volume per volume of rock, was carbon dioxide. Powder from the same specimen of diabase, not treated with acid, yielded 8.51 volumes of carbonic anhydride in the combustion-tube. This amounted to 61.25 per cent of the total gas.<sup>2</sup>

While carbon dioxide, both gaseous and liquid, occurs in minute cavities in certain minerals and rocks, and while rocks also, doubtless, contain some of this gas in a state of occlusion, it seems probable, on account of the wide dissemination of carbonates in small quantities through the accessible rocks near the earth's surface, that the greater part of the carbon dioxide obtained by the method of heating rock material in vacuo is derived from the decomposition of carbonates in the combustion-tube. It may be assumed that more of the carbonates in igneous rocks are secondary than primary. But though a knowledge of this immediate source of much of the carbon dioxide in the rocks does not lead far toward the elucidation of the problem of the ultimate source of this gas, it imposes no restrictions upon the more comprehensive view that the carbonic acid which is now locked up in the rocks chemically, as a result of weathering and carbonation, was given to the atmosphere and hydrosphere originally from the magmas themselves.

## CARBON MONOXIDE.

Metallic iron and ferrous salts reduce carbon dioxide to monoxide under practically the same conditions that they liberate hydrogen from water-vapor.

$$3\text{FeO} + \text{CO}_2 = \text{Fe}_3\text{O}_4 + \text{CO}$$

While this action commences below 400°, it takes place slowly, and it is chiefly at higher temperatures that it becomes of quantitative importance. As in the case of hydrogen and water-vapor, this reaction is reversible, the direction in which it will proceed depending upon the proportions of the substances present. Either metallic iron or ferric oxide, heated in a mixture of equal parts of carbon monoxide and carbon dioxide, produces ferrous oxide. Siderite at red heat passes into a magnetic oxide with the formation of both carbonic acid and carbonic oxide. Döbereiner this reaction takes place as follows:2

$$5$$
FeCO<sub>2</sub> =  $3$ FeO.Fe<sub>2</sub>O<sub>3</sub> +  $4$ CO<sub>2</sub> + CO

Glasson, however, says that 4FeO.Fe,O, results, at first giving two parts of CO<sub>2</sub> and one of CO, but that later the proportion changes to five parts of CO<sub>2</sub> and one of CO.

It is, therefore, the normal thing for a rock containing carbon dioxide (whether occluded, or in cavities, or a carbonate) and iron in the ferrous condition to generate carbon monoxide on the application of heat. In this connection it may be noted that carbon monoxide rises very conspicuously in relative importance whenever there is metallic iron present in the material tested. The iron-bearing basalt of Ovifak, Greenland, gave 21.63 per cent of this gas compared with 46.50 per cent of the dioxide, the Allegan meteorite, 38.61 per cent of CO and 41.74 per cent of CO<sub>2</sub>;4 while the Estacado meteorite developed 29.31 per cent monoxide and only 28.47 per cent dioxide. These were specimens of stony material containing grains of metallic iron. Quite different is the Toluca iron meteorite, whose nearly pure metal evolved 71.05 per cent carbonic oxide with but 6.40 per cent carbonic anhydride. Wright's figures for iron meteorites are equally noted for high percentages of carbon monoxide.

However, there are two other chemical sources for carbon monoxide, one of which is, perhaps, especially applicable to iron meteorites. It is known that the carbides of chromium and iron, when heated with the oxides of these metals, produce carbonic oxide.8 As these meteorites often contain considerable carbon, some of it perhaps as a carbide, scrupulous care is always necessary in preparing the metal for the analysis, to avoid introducing any rust from the oxidized exterior of the mass.

The other principle must always be operative in the combustion-tube. Boudouard has shown that at the temperatures of the combustion-furnace hydrogen reduces carbon dioxide, forming carbon monoxide at the expense of both hydrogen and the dioxide.

Wright and Luff, Jour. Chem. Soc., vol. 33 (1878), p. 504.
 Cited by Gmelin-Kraut, Anorg. Chem., vol. 3, p. 319.
 Analysis No. 45.
 Analysis No. 106.
 Analysis No. 107.
 Analysis No. 108.
 See p. 6.
 Borchers and McMillan, Electric Smelting and Refining, p. 545.
 O. Boudouard, Chem. Central-Blatt (1901), 1, p. 1350.

$$CO_2 + H_2 = CO + H_2O$$

Equal volumes of hydrogen and carbon dioxide heated at 850° for one hour gave CO<sub>2</sub> 44.3 per cent, CO 8.3, H<sub>2</sub> 42.0, and H<sub>2</sub>O 5.4 per cent. Heated for three hours under the same conditions, the proportion of carbon monoxide rose to 18 per cent. When rocks are heated for analysis, the gas is usually pumped off at short intervals, and this reaction, because of its slowness, becomes less important. Huttner has appealed to this reaction to explain the presence of carbon monoxide in minerals.

But metallic iron also has a penchant for absorbing carbon monoxide at the proper temperature. This process is usually called occlusion, and may perhaps partake of the nature of a combination in which the gas temporarily unites with the iron as iron carbonyl, Fe(CO)4,1 an unstable compound readily giving up carbonic oxide. It seems likely that a portion of the carbon monoxide developed from these irons, particularly those of meteoritic origin, actually exists in the iron as monoxide, and that not all of it has been formed by reduction of the dioxide.

#### SULPHUR DIOXIDE.

Certain rocks, when heated, disengaged sulphur dioxide in considerable quantities.2 These were ferruginous rocks of rusty appearance, generally metamorphosed pyritiferous shales which had undergone much weathering. By oxidation, the original pyrite had been partially converted into ferrous sulphate (FeSO4) and basic ferric sulphate (Fe2S2O9), both of which were decomposed by the heat of the combustion-furnace.

$$2\text{FeSO}_4 = \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$$
  $\text{Fe}_2\text{S}_2\text{O}_9 = \text{Fe}_2\text{O}_2 + 2\text{SO}_3$ 

The sulphur trioxide was reduced to the dioxide either by hydrogen sulphide, hydrogen, ferrous oxide, or sulphur.

$$SO_3 + H_2S = SO_2 + H_2O + S$$

It has been my observation that whenever sulphur dioxide was evolved a slight sublimate of sulphur collected toward the cool end of the tube. This may have been derived from the reaction above, or from hydrogen sulphide and sulphur dioxide, coming from ferrous disulphide and sulphate, respectively, and which can not exist together.

$$2H_2S + SO_2 = 2H_2O + 3S$$

The sulphur dioxide obtained in the study of rocks is all assigned to these reactions, though it is not impossible that this compound may occur in small quantities, as a gas or a liquid, imprisoned in minute cavities.

## HYDROGEN SULPHIDE.

When iron pyrites (FeS<sub>2</sub>) is heated in a stream of hydrogen, ferrous sulphide (FeS) and free sulphur result.<sup>3</sup> Though no hydrogen sulphide

Fe and CO also exist feebly united in other proportions, as iron pentacarbonyl, Fe(CO)<sub>5</sub>, and heptacarbonyl, Fe(CO)<sub>7</sub>.
 Analyses Nos. 43, 65, 93, and 109.
 Rose, Pogg. Ann., vol. 5, p. 533.

is formed in this manner, that gas is produced when pyrite is decomposed by steam at high temperatures.1

$$FeS_2 + H_2O = FeO + H_2S + S$$

As pyrite is frequently present in igneous rocks which generally evolve water-vapor upon the application of heat, the limited quantities of hydrogen sulphide obtained may be explained in this way. But unless the hydrogen sulphide be removed, this process can proceed only to a certain point, for, according to Berzelius, iron disulphide is formed when FeCO<sub>s</sub>, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, or Fe(OH)<sub>3</sub> is heated with hydrogen sulphide to temperatures between 100° and red heat.<sup>2</sup> At red heat, a current of dry hydrogen sulphide completely converts Fe<sub>3</sub>O<sub>4</sub> into Fe<sub>3</sub>S<sub>4</sub> in two hours, while a still further increase of temperature results in the formation of FeS and a deposit of sulphur.8

An inspection of the analyses shows that sulphureted hydrogen is rarely obtained in large amounts from igneous rocks. An average of 75 analyses from a wide range of rocks (but omitting bituminous shales) gave 0.59 per cent of this gas. But this figure is not a good working average, since it has been much influenced by the high sulphide percentage of a few individuals. Deducting the five highest of these, the remaining 70 analyses give an average of 0.27 per cent of hydrogen sulphide. In 19

cases out of the 75, this gas was entirely lacking.

While it is probable that not much of this gas was given off from the rock material in the first place, a portion of it doubtless disappeared before passing through the pump into the gas-receiver. At the temperature of the combustion-furnace, hydrogen sulphide is apt to be partially dissociated into its elements, thus swelling the already large volume of hydrogen present.4 Gautier states that sulphur heated in a tube filled with hydrogen sulphide causes the decomposition of the gas with the result that its sulphur is added to the free sulphur, while hydrogen, nearly pure, remains.5 When the rock has been considerably weathered, and some of the pyrite oxidized into iron sulphate, so that, in addition to hydrogen sulphide, sulphur dioxide is disengaged, the former gas will be partially or completely decomposed, depending upon the relative proportions of the two gases.

 $2H_2S + SO_2 = 2H_2O + 3S$ 

The bituminous shale from Newsom's Station, near Nashville, Tennessee, yielded sulphureted hydrogen to the extent of 30.94 per cent of the total gas, which is equivalent to the unusual amount of 29.38 volumes of hydrogen sulphide from one volume of shale. A specimen of the well-

With an excess of steam the reaction goes further: 3FeS<sub>2</sub>+4H<sub>2</sub>O = Fe<sub>2</sub>O<sub>4</sub>+3H<sub>2</sub>S

<sup>1</sup> With an excess of second the Hamiltonian of the Hamiltonian excess of second excess of second excess of second excess of the Hamiltonian excess of second excess of the Hamiltonian excess of second excess of the Hamiltonian excess of the Hamiltonian excess of second excess of the Hamiltonian excess of second exce

known "oil rock" from a lead and zinc mine near Platteville, Wisconsin, produced 6.79 per cent hydrogen sulphide, corresponding to 3.90 volumes per volume of rock. How prolific a source of hydrogen sulphide the organic matter in certain shales may be, is indicated by these two experiments. If a shale of this sort, undergoing extensive metamorphism, did not lose all of its sulphur compounds during the transforming process, the metamorphic product might still be distinguished by a high content of hydrogen Perhaps the specimen of Baltimore gneiss obtained from Spring Mill, on the Schuylkill River,2 from which 4.91 per cent, or 0.30 volume, of sulphureted hydrogen was extracted, may have been derived from such a shale. Other sulphur compounds in small amounts have been noted in the gases from rocks. The potassium hydroxide solution in the Lunge nitrometer, after having absorbed whatever hydrogen sulphide and carbon dioxide there may have been in the gas under analysis, frequently emits an odor suggesting a mercaptan. When air is let into the pump and tubes, after the removal of the gas for analysis, and then pumped out, it usually is charged with odors of more or less offensive nature. These suggest that other complex reactions prevail at the high temperatures employed in extracting the gas. Gautier detected a trace of ammonium sulphocyanide in the gas from a granitoid porphyry from Esterel.<sup>3</sup>

#### METHANE.

Moissan believed that the hydrocarbons of the petroleum type which occur in the earth's crust were, in many cases, derived from the action of water upon metallic carbides in the deep interior.4 His important researches upon carbides form the experimental basis for the hypothesis that the methane obtained by heating igneous rocks has resulted from these compounds. Even with cold water, the carbides of barium, strontium, calcium, and lithium give pure acetylene, while under the same conditions aluminum and beryllium carbides generate pure methane.

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$
  $Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4$ 

The carbides of the rarer metals, cerium, lanthanum, yttrium, and thorium, yield various mixtures of acetylene and marsh-gas; from manganese carbide, marsh-gas and hydrogen result. But the most remarkable of the carbides is that of uranium, which with water at ordinary temperatures produces (in addition to a gaseous mixture of methane, hydrogen, and ethylene) both liquid and solid hydrocarbons. Under ordinary conditions water does not decompose the carbides of molybdenum, tungsten, chromium, or iron.

These reactions suggest two alternative hypotheses to explain the occurrence of methane in the gas obtained from igneous rocks. The most limited of these supposes the marsh-gas to be produced from a carbide

Analysis No. 42.
 Analysis No. 28.
 Gautier, Comptes Rendus, vol. 132, pp. 61–62.
 Moissan, Proc. Roy. Soc., vol. 60 (1897), pp. 156–160.

in the combustion-tube. Such a carbide must have withstood the action of water, both magmatic and meteoric, ever since the solidification of the The other hypothesis seeks to avoid this difficulty by postulating carbides in the very hot rocks where the hydrogen and oxygen may not be combined as water; then, at a later stage, it allows water to decompose the carbides with the evolution of marsh-gas, which is retained within the rock. In this case the gas itself would exist in the rock specimen tested.

It is to be noted that several of these carbides, including that of the widespread element calcium and the less stable sodium and potassium compounds,1 give acetylene when decomposed by water. In none of the rocks examined, with one exception, has acetylene been detected. may possibly eliminate calcium carbide from the gas-contributing compounds in the rocks. The absence of acetylene also carries with it some slight evidence against carbides in general, since calcium plays a very important rôle in rock evolution, and it is not likely that acetylene, if formed, would pass into methane. However, it is not impossible that aluminum carbide, which yields methane with water, may exist in the earth's crust while calcium carbide is lacking. According to F. W. Clarke,2 aluminum constitutes 8.16 per cent of the solid crust of the earth, while iron and calcium comprise 4.64 and 3.50 per cent, respectively. Aluminum also forms very stable compounds in nature. Moreover, aluminum oxide fused in the electric furnace with calcium carbide gives yellow crystals of Perhaps at high temperatures iron carbide might aluminum carbide. be decomposed by steam with the formation of marsh-gas.

Besides carbides, organic matter suggests itself as a possible source of the methane. This organic matter may have been either (1) accidentally introduced into the combustion-tube, or (2) have been incorporated in the rocks from life which inhabited the earth during the later stages of growth, as outlined by the planetesimal hypothesis. The first possibility may be practically dismissed, since great care was exercised to avoid the introduction of any foreign matter with the rock powder. If dependent upon such accidental conditions, this gas would only occasionally be present. Under the planetesimal hypothesis, life may have existed long before the growth of the planet was completed and its present size attained. Organic deposits buried in sedimentary beds which have since undergone extensive metamorphism should furnish marsh-gas. These rocks, worked over and reworked by the volcanic activity in Archean times, might perhaps account for the widespread occurrence of this gas. Formed in this way, it may be retained in the rocks as a free or occluded gas, since it is very stable at high temperatures.

Other theoretical sources of methane are high-temperature reactions within the combustion-tube, in which hydrogen and the oxides of carbon participate. Brodie produced 6 per cent of marsh-gas by submitting

Moissan, Jour. Chem. Soc., vol. 64, 2, p. 332.
 F. W. Clarke, Bull. 168 U. S. G. S. (1900), p. 15.
 Moissan, Comptes Rendus, 125 (1897), pp. 839-844; Jour. Chem. Soc., vol. 64 (1898), 2, p. 161.

approximately equal volumes of hydrogen and carbon monoxide to the action of electricity for five hours in an induction-tube.1 From his results he expressed this reaction by the equation,

$$CO + 3H_2 = CH_4 + H_2O$$

Though it is not safe to assume that this reaction will take place at the temperatures of the combustion-furnace, the observation that marsh-gas is obtained when a rock powder, exhausted of its gases, is exposed to the air for a few months, and reheated, possibly points toward some reaction of this nature.

#### NITROGEN.

If the nitrogen which is obtained from heating igneous rock powders in vacuo is derived from some chemical compounds decomposable at red heat, a metallic nitride at once suggests itself as the most probable form in which the nitrogen would occur. Iron nitride may be taken as the type for discussion. While different nitrides of iron, having the compositions of Fe<sub>2</sub>N<sub>2</sub>, Fe<sub>2</sub>N, and Fe<sub>5</sub>N<sub>2</sub>, have been described by some authors, a comprehensive study, by Fowler, of this formerly little-known compound, forces the conclusion that there exists 2 only one iron nitride, Fe<sub>2</sub>N. This compound may be prepared by the action of ammonia either upon ferrous chloride, or finely divided iron. While the action between ferrous chloride and ammonia commences near the melting-point of lead (327°), a temperature of 600° appears to be necessary for the production of iron nitride in quantity.3 The nitride can also be produced at 850° to 900°, but this is probably the highest limit of the reaction.4

This nitride is very soluble in dilute acids, giving ammonia. heated to redness in hydrogen, ammonia results. At 200° it is oxidized in the air to ferric oxide, abandoning nitrogen, which does not appear to be oxidized. At 100° steam causes a slight evolution of ammonia. According to Fowler the temperature of decomposition of iron nitride in an inert gas (nitrogen) must certainly be above 600°.

Silvestri has found iron nitride coating some of the fumarole deposits of Etna, and Boussingault recognized nitrogen in the Lenarto meteorite by certain tests which led him to believe that it existed there as a metallic nitride. Silvestri discovered that at red heat the nitride from Etna was decomposed, delivering up its nitrogen. His experiments showing that iron nitride may be prepared artificially, by igniting the ordinary lava in a current of ammonium chloride vapor, probably illustrate what takes place in the fumaroles. But this nitride, which derives its nitrogen from ammonia or ammonium salts, in no way requires the existence of nitrides within the magma itself, except as a possible source for the nitrogen which unites with hydrogen to form the ammonia. There is danger in transferring the characteristics of fumarole deposits, which are formed

Sir B. C. Brodie, Proc. Roy. Soc., vol. 21 (1873), p. 245.
 Fowler, Jour. Chem. Soc., vol. 79 (1901), pp. 285-299.
 Fowler, Chem. News, vol. 82 (1900), p. 245.
 Beilby and Henderson, Jour. Chem. Soc., vol. 79, p. 1245.
 Silvestri, Pogg. Ann., vol. 157 (1876), pp. 165-172.
 Boussingault, Comptes Rendus, vol. 53 (1861), pp. 78-79.

in limited quantities under the quite exceptional conditions of abundant currents of free gases and very active hot vapors, to the main magmas.

If the nitrogen obtained from rock powders be derived from a nitride, it should be accompanied by ammonia, since, in the presence of hydrogen or water-vapor, it is this gas, rather than free nitrogen, which is given off. Tests made with Nessler's solution show that ammonia is one of the gases extracted from rocks, though always appearing in limited amounts. In the process ordinarily employed for extracting the gas, it is absorbed by the calcium chloride drying-tube. Ammonia is scarcely to be considered as a source of free nitrogen, since this compound is only dissociated at the temperature of the electric spark.

Whether all of the free nitrogen can be assigned to the decomposition of iron nitride may be tested with the quartz from New South Wales.¹ Supposing all of the iron in this quartz to have existed as iron nitride, and to have been completely decomposed without the production of any ammonia, the analysis still shows an excess of nitrogen over what could have been produced in this way. The reaction may be taken as

## $2Fe_{2}N = 4Fe + N_{2}$

102.72 gms. quarts contained	0.0058 gm. Fe
Fe (as Fe <sub>2</sub> N) required to give 1 c.c. nitrogen	.0100 gm.
Nitrogen possible from reaction	.58 c.c.
Nitrogen actually obtained (0° and 760 mm.)	.86 c.c.
Excess of nitrogen	.28 c.c.

A duplicate determination of the iron in this weight of quartz gave only 0.0048 gram; on this basis, the excess of nitrogen would be still greater. It is highly improbable that all of the iron in this quartz was combined as a nitride. Some of it was unquestionably pyrite. To ascertain how much of this nitrogen can be ascribed to atmospheric air adhering to the tubes, as well as to leakage during the process of extraction, a blank combustion was resorted to. The empty combustion-tube was kept at bright-yellow heat for the length of time which was required to expel the gas from the quartz. 0.15 cubic centimeter of gas was collected in the receiver when the tube was exhausted by the pump. Adhesion of air to the quartz itself might be supposed to increase this figure, though the material used for this analysis was not the usual fine powder, but small fragments which would be less liable to entrap air. In general, while iron nitride is to be accepted as a possible source of this nitrogen, it is inadequate to produce the quantities of this gas determined by analysis. The presence of other metallic nitrides in this comparatively pure quartz does not seem likely. Silicon nitride, however, may be present and might possibly contribute a portion of the nitrogen.

## OCCLUDED GASES.

Though occlusion is a phenomenon but imperfectly understood, there appear to be three different ways in which it is manifested. In the first of these the absorption seems to be dependent upon porosity. An example of this is charcoal, one variety of which absorbs 172 volumes of ammonia,

165 volumes of hydrogen chloride, 97 volumes of carbon dioxide, and 2 volumes of hydrogen. The affinity of molten silver for oxygen illustrates another phase of absorption often classed as occlusion. It has long been known that silver absorbs 22 times its own volume of oxygen when melted, but gives up most of this gas, often with violence, as it solidifies.2 This is properly a solution of a gas in a liquid, and not in a solid, as in the case of true occlusion. The third type is the absorption of gases by compact metals, either on their surface or within their mass, such as the occlusion of hydrogen by palladium, platinum, and iron. This is, in the main, independent of porosity.

Hydrogen is absorbed by these metals at ordinary temperatures, but is only given off at higher temperatures. This principle was demonstrated by Graham, who placed a thin plate of palladium, charged with hydrogen, in a vacuum and observed that at the end of two months the vacuum was still perfect. No hydrogen had vaporized in the cold, but on the application of a heat of 100° and upwards, 333 volumes of gas were evolved from the metal.3 The degree of heat required to expel hydrogen absorbed by platinum and iron was found to be little short of redness, although the gas had entered the metal at a low temperature. Another series of experiments by the same investigator showed that, to be occluded by palladium and even by iron, hydrogen does not need to be applied under sensible pressure, but on the contrary, when highly rarefied, it is still freely absorbed by these metals. These results have been confirmed by Mond, Ramsay, and Shields,4 who found that platinum black at very low pressures absorbed a certain quantity of hydrogen. On increasing the pressure of the hydrogen up to about 200 to 300 millimeters, a further quantity was absorbed, but beyond this point an increase of pressure had comparatively little These investigators regarded 110 volumes as the amount of hydrogen really occluded by platinum black, although 310 volumes were actually absorbed.

Experiments indicate that the quantity of hydrogen occluded depends greatly upon the condition of the metal. When chemically reduced, cobalt may occlude 59 to 153 volumes, nickel 17 to 18, and iron 9 to 19 volumes. Though common iron wire occludes only 0.46 volume of hydrogen, this same metal, when electrolytically deposited, may absorb nearly 250 volumes of this gas. The maximum quantity of hydrogen occluded by any metal, so far as recorded, is 982 volumes absorbed by freshly precipitated palladium.8 Dumas has shown that aluminum heated in vacuo to 1400° gives off more than its own volume of gas, consisting chiefly of hydrogen with a little carbon monoxide, but without traces of carbon dioxide, oxygen, or nitrogen. Under the same conditions, magnesium rapidly expels 1.5

Barker, Textbook of Physics, p. 183.
 Chimie Minérale, Moissan, t. 1, p. 203.
 Graham, Chemical and Physical Researches, pp. 283-290.
 Proc. Roy. Soc., vol. 58 (1895), pp. 242-243.
 Chimie Minérale, Moissan, t. 1, p. 51.
 Graham, Chemical and Physical Researches, p. 279.
 Cailletet, L'Institut, Nouv. Sér., Ann. 3, p. 44.
 Graham, Chemical and Physical Researches, p. 287.
 Dumas, Comptes Rendus, 90 (1880), p. 1027.

volumes of nearly pure hydrogen. Many other metals behave similarly. Non-metallic substances appear to possess this property in a lesser degree. Porcelain occludes hydrogen, whether because of its porosity or solvent qualities is not certain. Quartz is said to be penetrable, at high temperatures, by the gases from the oxyhydrogen flame, which points towards a form of occlusion.

In addition to hydrogen, other gases are occluded. Litharge, when in the molten condition, dissolves hydrogen, carbon monoxide, and nitrogen, of which it retains a portion on solidifying.2 Cast iron, on cooling, retains 4.15 volumes of carbon monoxide, which perhaps may be due to the formation of iron carbonyl, Fe(CO)<sub>4</sub>, or similar unstable compounds.

Analyses show that whenever metallic iron is present in notable quantities carbonic oxide becomes an important constituent of the gas evolved. The following analyses of the gases from various types of iron indicate the proportions of hydrogen, carbon monoxide, carbon dioxide, and nitrogen which this metal may absorb, given in percentages of the total gas content:

TABLE 36.

Iron.	Analyst.	H <sub>2</sub> .	co.	CO <sub>2</sub> .	N <sub>2</sub> .
White, carbonaceous, cast iron	Troost & Hautefeuille <sup>1</sup>	74.07	16.76	3.59	5.58
Mild steel	Parry	52.6	24.3	16.55	6.5
Ordinary gray charcoal iron	Cailletet	38.60	49.20		12.20
Gray coke iron	Do	32.70	57.90	••••	8.40
Steel					
	Hautefeuille	22.27	63.65	2.27	11.36
Bessemer steel before adding spiegel	Müller <sup>2</sup>	88.8	0.7		10.5
Bessemer steel after adding spiegel	Do	77.0			22.9
Open-hearth steel	Do	67.8	2.2	• • • • •	30.8
Cupola pig iron	Do	83.3	2.5		14.2
Horseshoe nail, heated 2 hours	Graham <sup>2</sup>	35.0	50.3	7.7	7.0
Same, heated 2 hours more	Do	21.0	58.0	• • • • • • • • • • • • • • • • • • • •	21.0

Whatever may prove to be the ultimate significance of occlusion, and in whatever condition these gases are stored in the iron, whether it be in the nature of a solution, as Mendeléef has suggested, or as definite compoundshydrides, nitrides, and carbonyls—the fact remains that these gases exist within the metal and are in many respects similar to the gases locked up in iron meteorites. Fresh iron borings from the interior of a metallic meteorite have usually been assumed to be free from any hydration or carbonation from terrestrial agencies, and so have been held to contain true meteoritic gases. Some question respecting this belief has arisen from certain analyses which, as we have seen, indicate secondary action.4 In addition to this the gases actually received in the laboratory may not represent the original

<sup>&</sup>lt;sup>1</sup>Cited by Cohen, Meteoritenkunde, p. 181. <sup>2</sup>Cited by Lane, Bull. Geol. Soc., vol. 5 (1894), p. 264.

Poynting and Thomson, Properties of Matter, p. 204.
 Le Blanc and Cailletet, cited by Violle, Cours de Physique, t. 1, p. 922.
 Daniell, Principles of Physics, p. 327.
 Experiments with the Toluca iron; Analysis No. 108.

proportions on account of the reducing action of iron on carbon dioxide and water-vapor. Meteorites of the stony type, unless absolutely fresh, are more open to the suspicion of terrestrial hydration and carbonation. But the Allegan meteorite gathered up, still hot, within five minutes of its fall, has not been subjected to outdoor exposure, though it may have absorbed a small amount of moisture and carbonic acid from the atmosphere since being placed in the National Museum. It yielded somewhat more than half of its own volume of gas.¹ Fresh material from the interior of the Estacado, Texas, meteorite, heated in a vacuum in the presence of phosphorus pentoxide for five hours at 150°, and then allowed to remain untouched for several days to enable the drying agent to take up the last traces of moisture in the tubes, still yielded at red heat 0.86 volume of gas, of which 36.25 per cent was hydrogen.2

These gases from stony meteorites resemble those from some igneous That this correspondence should exist, is entirely in accordance with the view that meteorites have been derived from the disruption of small planetary bodies of the nature of the asteroids. As in the meteorites, so in the rocks, that portion of the gases which can not have been produced by chemical reactions at elevated temperatures, nor from the bursting of rock-bound cavities, may fairly be assigned to occlusion. The computations indicating the excess of hydrogen obtained from quartz and beryl \* over that which might have arisen from the interaction of iron and water under the most generous assumptions show that, in some cases, more gas may arise from a state of occlusion than from ordinary chemical action. The amount of occluded gases may be actually greater than that indicated by demonstrating the inadequacy of other modes of holding gas. But in basic rocks containing hydrated minerals and an abundance of ferrous salts, the resulting volumes of hydrogen must doubtless come largely from the decomposition of the water of constitution, and the amount of occluded gases, if any, is beyond determination by these methods.

The gases argon and helium, which, according to current chemical views, do not form compounds, must exist within rocks either mechanically entrapped or in a state of occlusion. There are those, notably Ramsay and Travers, who believe in the combining properties of argon and helium; but the balance of opinion seems to be on the other side, so far as ordinary terrestrial conditions are concerned. Lord Rayleigh concludes his paper on the inactivity of these two gases, with this sentence: "There is, therefore, every reason to believe that the elements, helium and argon, are nonvalent, that is, are incapable of forming compounds."4

As the chemists' supply of helium comes from certain minerals, chiefly those containing compounds of uranium, its occurrence in rocks is a wellknown fact. Recent studies have revealed the existence of helium in beryl.5 Argon is perhaps more widely distributed than helium, Gautier having detected this element in ordinary granite. The waters of many springs

<sup>&</sup>lt;sup>1</sup> Analysis No. 106.

<sup>&</sup>lt;sup>2</sup> Analysis No. 107.

<sup>&</sup>lt;sup>8</sup> Ante, pp. 46–48.
<sup>4</sup> Lord Rayleigh, Proc. Roy. Soc., vol. 60, p. 56.
<sup>5</sup> R. J. Strutt, Nature, Feb. 21, 1907, p. 390.

bring up both helium and argon, proving the presence of considerable quantities of these elements within the earth. This rather wide distribution, when taken in connection with their supposed chemical inertness, strengthens the presumption that occlusion, or some form of gas diffusion, is prevalent in rocks. Though of much interest to chemists and physicists, these gases, on account of their comparative scarcity, do not play a very important rôle in general geological problems. Their presence in small quantities within the rocks of the earth's crust being established, quantitative determinations become of less value. In the analyses made for this paper, whose prime purpose was to determine the range and distribution of the common gases, the separation of helium and argon from nitrogen was not usually attempted. These gases when present are included in the figures given for nitrogen. In the case of pitchblende and carnotite, however, helium was so important a constituent of the gas that its proportions were determined. Carnotite produced 1.28 per cent of helium, amounting to 0.04 volume, while pitchblende gave 38.48 per cent, or 0.37 volume. In both of these cases nitrogen also was abnormally high.

In general, therefore, helium and argon, together with at least as much of the other gases as can be shown not to have been produced by chemical reactions or the bursting of inclosing walls, are to be attributed to occlusion or some form of diffusion not distinguishable from occlusion. In many, and perhaps most, rocks this will not be the major part, for, of the three gas-liberating processes, that by chemical interaction under the influence of heat appears to be the dominating one.

# SIGNIFICANCE OF THE THREEFOLD STATE.

GAS IN CAVITIES.

While chemical reactions and the phenomena of occlusion imply that gas exists in the interior of the earth, the presence of gas inclosed in cavities under great pressure adds the further implication that the gas often exceeded the point of saturation of the magma, at least at the stage of solidification. Cavity gases are most abundant in minerals of poorly developed cleavage, pointing perhaps towards a strong tendency to escape along cleavage planes during, or after, crystallization. The gas inclusions in quartz may, however, owe their abundance not so much to the absence of cleavage as to the fact that quartz is generally the last mineral to crystallize out of a magma, and hence such absorbed gases as did not enter into the other crystals would become concentrated in the siliceous residue and might supersaturate it.

It is possibly this freely-moving gas above the point of saturation which contributes most to the mobility of lavas. Dissolved gases and vapors, while favoring fluidity, would seem to be relatively less effective. But the foregoing investigations imply that gases mechanically entrapped in crystalline rocks are not very abundant, and suggest that perhaps the theory of liquidity due to gas is overworked. On the other hand, it is true that as the lava cooled down to the point where the last mineral crys-

<sup>&</sup>lt;sup>1</sup> Analyses 93 and 94.

tallized, its gas-solvent powers would be increasing, allowing some of the gas to pass into solution. At the same time free gas might be occluded by the growing crystals. The experiments upon the reabsorption of gas by exhausted rock powder indicate that a portion of the gas unites chemically as the heat diminishes. Because of these processes, liquid lavas may be supplied with free gas, even when the solidified rocks retain but little free gas.

As the imprisoned carbon dioxide frequently remains in the liquid form up to the critical point (30.9° C.), it must be subjected to a pressure of at least 73 atmospheres, which is the critical pressure of this gas. Since a pressure of 73 atmospheres corresponds to a column of water 2,470 feet in height, quartz crystals formed from aqueous solution, under hydrostatic pressure simply, can not contain liquid carbon dioxide up to 30.9° unless developed at depths exceeding 2,470 feet. It is to be recognized, however, that such crystals might be formed at lesser depths if mechanical pressure operated with hydrostatic pressure or replaced it.

If the quartz crystallized from a lava, say at 1100° C., the effect of cooling down to ordinary temperatures upon both the size of the cavity and the pressure of the inclosed carbon dioxide must be taken into account. If we take the case of a cavity found to be entirely filled with carbon dioxide at the critical point (30.9° C. and 73 atmospheres), it is possible, by the use of Van der Waal's equation, to calculate the pressure to which the gas would be subjected if the quartz were heated to 1100°. This pressure is found to be 756 atmospheres,1 provided the size of the cavity remains constant. But as most minerals contract on cooling, the volume of the cavity diminishes at the same rate as though it were filled with the material of the inclosing walls.2 The coefficient of expansion of quartz is given as 0.00003618. Assuming for the sake of simplicity that the rate of expansion does not vary greatly with changing temperatures,3 quartz, cooling from 1100° to 31°, would contract to an extent of about 3.87 per cent of its original volume. Since the contraction of the quartz diminishes the size of the cavity and increases the pressure by 3.87 per cent, the original pressure need be only 727 atmospheres, which corresponds to the pressure beneath 9,100 feet of average rock. To fill cavities forming in crystals at 1100° with carbon dioxide which is so condensed that it will pass into the liquid state just at the critical temperature when the rock cools down, a pressure corresponding to a depth of at least 9,100 feet, or its mechanical equivalent, would seem to be required. If, when warmed under the microscope, the liquid carbon dioxide is found to pass into the gaseous state at temperatures below 30.9°, and the cavity contains only carbon dioxide, or carbon dioxide and water, these must have been entrapped under a pressure less than 727 atmospheres, or else the crystal was formed at a temperature above 1100°.

<sup>&</sup>lt;sup>1</sup> By starting with the equation  $p = \frac{RT}{v-b} - \frac{a}{v^2}$  at the critical point where the values of the constants are taken as R=0.003684; a=0.00874; b=0.0029; v=3b=0.0087, and substituting for the critical temperature,  $T=1100^\circ+273^\circ$ , the theoretical value of 756 atmospheres for the pressure at 1100° is obtained.

<sup>2</sup> Daniell, Principles of Physics, p. 379.

<sup>3</sup> It would, however, slowly increase with the increase of temperature.

The estimate of 9,100 feet for the minimum depth (where weight alone acts) at which igneous quartz crystals now containing carbon dioxide, liquid up to 30.9°, could have been formed,¹ applies best to those cases in which only carbon dioxide exists in the crystal cavities. If there are other gases and liquids present in appreciable quantities, this figure becomes less applicable, since the constants a (denoting an internal force or attraction) and b (representing the sum of the spheres of influence of all the molecules in the space v) used in Van der Waal's equation are not the same for all gases. At how much greater depths than this the crystallization of certain specimens of quartz actually did take place, if rock weight alone was involved, may, perhaps, be estimated by a painstaking determination of the pressure under which the imprisoned carbon dioxide exists in these minute cavities. This might be accomplished by piercing one of the larger cavities while submerged in mercury or other liquid, and noting the expansion of the freed bubble, as first suggested by Sir Humphry Davy.

Though naturally subject to limitations, it is nevertheless possible to throw considerable light upon the nature of cavity inclusions by the use of the microscope. Some of the conditions may be stated:

(1) If, at slightly under 30.9°, the cavity is entirely filled with a liquid which completely vaporizes at 30.9°, it contains only carbon dioxide.

(2) If, at slightly under 30.9°, the cavity is filled with two immiscible liquids, one of which passes into the gaseous state at 30.9°, the liquids are probably water and carbon dioxide.

(3) If the cavity, when just below 30.9°, contains a liquid and an appreciable gas-bubble, and the liquid does not disappear when the slide is warmed above 30.9°, the liquid is probably water, and the bubble water-vapor with perhaps some of the difficultly liquefiable gases, such as hydrogen, nitrogen, or methane.

(4) If, as is often the case, the temperature at which the liquid in a cavity disappears is found to be several degrees below the critical temperature of carbon dioxide, two interpretations are possible: either the carbon dioxide is subject to a pressure less than 73 atmospheres, or else there is a small proportion of another less liquefiable gas present. If the cavity be opened and only carbon dioxide be found, the pressure under which the gas existed, and from that something as to the conditions under which the crystal was formed, can be computed from the temperature at which the liquid disappeared. If another gas, such as hydrogen or nitrogen, be found and identified, it is possible, by using an equation, to calculate the relative proportions of the two gases from the critical temperature of the mixture. Thus a cavity containing a mixture of carbon dioxide and nitrogen which had a critical temperature of 29° would hold 98.7 per cent

<sup>&</sup>lt;sup>1</sup> This figure is based on the assumption that the quarts crystallized at 1100°; if it is desired to use other temperatures, they can be substituted in Van der Waal's equation and the corresponding pressures computed.

<sup>2</sup>  $t = \frac{nt_1 + (100 - n)t_2}{100}$ , where t is the observed critical temperature of the mixture,  $t_1$ 

 $t_1 = \frac{n_1 + (100 - n) \cdot t_2}{100}$ , where t is the observed critical temperature of the mixture,  $t_1$  and  $t_2$  are the theoretical critical temperatures of the two liquefied gases. Then n equals the proportion by weight of the first liquid and 100 - n equals the proportion by weight of the second liquid.

of the former and 1.3 per cent of the latter. A critical temperature of 28° would indicate 98.1 per cent of liquid carbon dioxide and 1.9 per cent of liquid nitrogen, while 27° would mean 97.5 per cent of the dioxide and 2.5 per cent nitrogen. The figures for carbon dioxide and hydrogen are of the same general order. In the estimates of the depths at which cavity-bearing crystals were formed, made by different methods, it has been usual to assume that only the pressure arising from the weight of the overlying rock was involved.

Sorby examined those cavities which contained only water, or a saline solution, and a vacuole left by the contraction of the liquid, as a result of the lowering of the temperature. By noting the relative size of the bubble and the volume of the liquid, he estimated the temperature to which the mineral would have to be heated for the liquid to completely fill the cavity, and from this, together with the elastic force of the water-vapor, he computed the necessary existing pressure in feet of rock. The highest temperature found by this method was only 356° C., at which point Sorby believed that the trachyte of Ponza solidified, while the lowest temperature was 89° C., obtained from a study of the main mass of granite at Aberdeen. But Sorby considered it more probable that the granite crystallized at about the same temperature as the trachyte and, assuming that the solidification took place at 360°, he computed that the granite of Aberdeen was formed under a pressure of 78,000 feet of rock.<sup>2</sup> These estimates are based upon the unwarranted supposition that when the crystals were formed the volume of liquid water was such as to just fill the cavities, and that in each case a meniscus at once appeared with a loss of heat. He overlooked the fact that the meniscus could not appear until the water reached the liquid condition, no matter at what temperature the growing crystal surrounded the vesicle of highly compressed water-gas.

The highest temperature at which a vacuole of this sort can appear must, therefore, be the critical temperature for water, or 365° C. In order to study this problem, we may, perhaps, best take the special case in which the inclosed water passed through its critical state (at 365° and 200.5 atmospheres pressure) during the cooling of the crystal. The vesicle formed in this case may be termed the critical vacuole. It may be assumed that the growing crystal inclosed the water at some temperature in the neighborhood of 1100°, which is an average temperature for the solidification of lavas. Starting thus with a cavity formed at 1100°, in order to allow the water on cooling to pass through the critical state, an original pressure of 1,070 atmospheres is necessary according to Van der Waal's equation,3 provided the size of the cavity remained constant. But if 2.66 per cent is allowed for the shrinkage of the cavity while cooling down from 1100°

<sup>&</sup>lt;sup>1</sup> See Geikie's Textbook of Geology, vol. 1, pp. 144-145.
<sup>2</sup> Sorby, Quart. Jour. Geol. Soc. London, vol. 14, p. 494.
<sup>8</sup>  $p = \frac{RT}{v-b} - \frac{a}{v^2}$ . In this case the values of the constants for the critical point were taken to be R=.003607; a=.01173; b=.00151; v=3b=.00453. By substituting for the critical temperature, T=1100+273, the equation gives the theoretical value of 1,070 atmospheres.

Ante, p. 62.

to 365°, the original pressure need be only approximately 1,040 atmospheres, a pressure which corresponds to 13,000 feet of rock approximately.

In this critical case the meniscus appears as soon as the temperature falls below 365°. Since pressure exerts but little influence on the volume of liquids, the shrinkage of the water in the cavity, and hence the growth of the gas-bubble, is largely a function of the fall in the temperature, and, with a knowledge of the varying coefficient of expansion, the relation between the size of the bubble and the volume of the liquid could be computed for any temperature. The correction for the constriction of the cavity between 365° and 20° amounts to a little more than one per cent, which is to be added to the size of both the cavity and the vacuole in computation.

If these principles be true, a vapor-bubble relatively smaller than the critical vacuole may be interpreted to mean that the meniscus did not appear in the cavity until the crystal had cooled below the critical temperature, i.e., that at this temperature the water was more than normally condensed, owing to a pressure exceeding the critical pressure. On the other hand, a vapor-bubble relatively larger than the critical vacuole means that, although it did not appear until below 365°, it began as a sizable vesicle when it did start, owing to the lower pressure and more rarefied condition of the water-gas.

On the basis of his experiments, Sorby estimated that a vesicle amounting to 28 per cent of the volume of the liquid in the cavity would vanish when the water was heated to 340° C. According to this figure, a vacuole occupying in the neighborhood of 30 or 35 per cent of the volume of the liquid should correspond to a shrinkage of the water from the critical point to ordinary temperatures. But this figure has not been confirmed by other investigators. Unfortunately the figures obtainable for the expansion of water up to the critical point vary within such wide limits that it does not seem advisable at the present time to attempt to calculate the relative sizes of the critical vacuole and the inclosing liquid.

The difficulties involved in applying these principles are considerable. Zirkel has pointed out that, even in cavities within the same crystal, there is much variation in the relative volume of the vapor-bubble and the liquid, from which the inference is drawn that the vapor-bubbles are due to causes other than contraction on cooling.<sup>1</sup> Before this conclusion can be accepted with confidence, due consideration must be given to the location of the cavities within the crystal, and also to the evidence that they are all primary inclusions. In an ascending lava subject to a steadily diminishing pressure, those cavities formed during the early stages of crystallization may be developed under conditions quite different from the cavities later inclosed in the outer parts of the crystals. If systematic differences in the cavities can be found to correspond with variations in their location, something might be learned of the history of the lava during the period of crystallization. Secondary fluid inclusions, formed subsequent to the solidification of the magma, must obviously be recognized and avoided, whenever possible, in attempting to estimate the conditions under which crystallization took place.

<sup>&</sup>lt;sup>1</sup> Zirkel, cited by Geikie, Textbook of Geology, 1, p. 145.

A difficulty of a more serious nature, apparently, suggested by Professor Iddings, lies in the change of volume of the magma in the passage from the liquid to the crystalline form. Some magmas, such as those of granitic rocks, contract so appreciably upon crystallization that it is conceivable that the last crystals to form, those of quartz (which also contain the most liquid and gas inclusions) might crystallize under reduced pressures in spaces inclosed by crystals of the minerals already formed. The relative size of the bubble of vapor in the cavity and the accompanying liquid would, in such cases, not correspond directly to the depth beneath the surface at which crystallization took place, even when nothing but hydrostatic pressure affected the lava column.

In the present defective state of knowledge as to the modes and conditions which obtain in lavas penetrating the shell of the earth, it is by no means safe to assume that the pressures to which an igneous intrusion is subject are merely those represented by the overlying rock or a lava column reaching to the surface. An ascending tongue of lava may extend to great depths and be affected by pressures brought to bear upon it in its lower part, which might be in excess of those represented by the depth of the head of the column, to an unknown degree. So also it is possible that lavas may become involved in mechanical deformations and thus be subject to special pressures in no close correspondence to their depth.

#### WATER AND HYDROGEN.

The reversible reactions involving hydrogen, water, and iron compounds, which cause uncertainties in the extraction of gases by heat, are also operative within the earth. In the laboratory, when either ferrous salts and water, or ferric compounds and hydrogen, are heated in tubes without the removal of the products, reversible reactions set in until a condition of equilibrium is established. Hydrogen and water, ferrous and ferric salts are all present in a state of balance. In the interior of the earth the heated, though solid, rocks should, it would seem, behave similarly, though hindered by the slowness of diffusion. Nor should liquid magmas constitute any exception to the law. Both hydrogen and water-gas, theoretically, should be present in liquid magmas and heated solid rocks. The chief uncertain factors are high temperatures, and pressures.

The effect of pressure on chemical equilibrium is to favor the formation of that system which occupies the smaller volume, but if there is no change in volume, in passing from one system to the other, the increase of pressure presumably has no influence on equilibrium. In the reaction

$$3\text{FeO} + \text{H}_2\text{O} \iff \text{Fe}_2\text{O}_4 + \text{H}_2$$

considered as a thermochemical equation, the number of gaseous molecules, and hence the volume of gas, always remains the same, so that it is not likely that this action will be influenced by change of pressure. A rise of temperature favors the formation of that system which absorbs heat when it is formed.<sup>2</sup> A comparison of the amount of heat liberated by oxidizing three molecules of FeO to Fe<sub>2</sub>O<sub>4</sub> and one molecule of H<sub>2</sub> to H<sub>2</sub>O

Jones, Physical Chemistry, p. 514.
 Van't Hoff, Lectures on Theoretical and Phys. Chem., Pt. 1, pp. 161–164.

shows that, in the former case, 73,700 calories are evolved, and in the latter 58,300; that is,  $3\text{FeO} + \text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 + 15,400$  calories. As heat is evolved in this process, a rise of temperature would accelerate the reaction in this direction less than the reverse. In other words, the higher the temperature, the more would the formation of ferrous oxide and water be favored as compared with the conditions at lower temperatures.

Because of this, there is much reason to suppose that, at the depths where lavas originate, hydrogen and oxygen exist combined as water, since up to temperatures of 2000° C., the dissociation of water takes place only to a limited extent. If a state of equilibrium between hydrogen, water, and the iron compounds were established in the heated interior where a magma originated, as soon as it commenced its way upward and began to lose heat the condition of equilibrium would be destroyed. With the falling temperature, the tendency to reëstablish equilibrium would favor the formation of that system which was produced with the liberation of heat, i.e., magnetic oxide and free hydrogen. In ascending lavas which are losing heat, the tendency, therefore, is to produce hydrogen and magnetite, or ferroso-ferric compounds. This is doubtless an important source for the hydrogen which is so copiously exhaled during a volcanic eruption. At the same time, this process accounts for the widespread occurrence of magnetite in igneous rocks. The considerable deposits of magnetite, formed apparently from magmatic segregation, which are common in various regions, may, perhaps, owe their origin to a combination of causes, in which this equilibrium reaction is an important factor.

In general, these reversible reactions tend to show that it is but a short step from hydrogen to water, and from carbon dioxide to monoxide, and vice versa, and that all of these must occur within the earth owing to the processes tending toward equilibrium. Whether hydrogen, in a particular case, occurs in the magmas in the free state, or in the form of water-gas, therefore becomes relatively unimportant. Because of this variation of state, the problem becomes more complex and broader in scope. For the most part, these water-gases are to be regarded as truly magmatic, and not derived from surface-waters penetrating to the liquid lavas, as will be brought out later. They are here put forward as essential factors in the evolution of the magmas from the original planetary matter.

The reactions working towards equilibrium are able to supply hydrogen and carbon monoxide under conditions favorable to their absorption and retention, even if they were not originally present as occluded gases. The sources of the gases obtained from rocks are so complex that it is difficult to determine how much is to be assigned to each. Because of the penetration of surface-waters containing carbonic acid in solution, throughout the accessible rocks of the earth's exterior, it is likely that, in many cases, the bulk of the gas obtained by heating powders in vacuo has been derived from acquired water and carbonated compounds. But in fresh meteorites, which presumably have not been subjected to action of this sort, occlusion is relatively more important.

From the constitution of meteorites, some of the principles of early terrestrial evolution may, perhaps, be inferred, though the growth of the

earth was probably not quite analogous, in all respects, to the formation of the meteorites. Whether we take the meteoritic material to represent the heavier part of the original matter of the solar system, or the stellar system, as a whole, matters little in the geologic problem. If, in truth, the unoxidized, heterogeneously aggregated material of meteorites be typical of the original heavy material of the earth, it becomes evident that, in the case of our planet, other factors have been at work which are not operative in the bodies of which the meteorites are supposed to be fragments. These visitors from space are characterized by such minerals as cohenite, (Fe,Ni,Co),C, lawrencite, FeCl, oldhamite, CaS, and schreibersite, (Fe,Ni,Co),P, which, next to nickel-iron, is the most widely distributed constituent of iron meteorites,1 though of less importance in the stony specimens. Such compounds imply an absence of both free oxygen and water in notable quantities. Of like import is the absence of hydrated minerals, such as micas and amphiboles. Water and an oxygenated atmosphere appear to be the agents which are lacking in the bodies from which the meteorites were derived, but which have been the operative factors in working over the outer portion of the earth.

But the original source of the earth's atmosphere and hydrosphere is taken to be gas occluded, or absorbed, in the primitive meteoritic material. These original gases, escaping, furnished both atmosphere and hydrosphere when the earth became of sufficient size to retain them. A self-regulating system was inaugurated. In the early stages of the hydrosphere, when growth by infalling planetesimals was rapid, much water was buried within the fragmental crust. This material, worked over by volcanic activity, brought to the surface and subjected to weathering and erosion, and buried beneath more material, has undergone assortment and alteration until the accessible rocks at the present time are very different from the meteoritic matter. Since the earth attained its growth and the infall of planetesimals slackened, much less water has penetrated to great depths below the surface. Post-Archean sedimentaries have not yet reached thicknesses sufficient to carry inclosed water down to the depths from which the lavas arise. Deep mines indicate that fractures and fissures do not convey water down to very great depths at the present time. water does not penetrate so rapidly now, and hydration and carbonation are less effective, it is also probably true that subsiding vulcanism brings less gas to the surface.

It is essentially a system of balance. At the same time that water is being buried with sediment, its elements, hydrogen and oxygen, the latter in the form of the oxides of carbon, are exhaled from the earth's interior through volcanic outlets. But the system here suggested is very different from the postulated limited cycle of underground water which, following Daubrée's famous experiment,<sup>2</sup> has crept into geologic literature as the origin of volcanic vapors and the modus operandi of vulcanism. Instead of surface-waters following cracks and fissures down to the hot lavas there to be absorbed, the water already is present, and is a part of the rocks and

<sup>&</sup>lt;sup>1</sup> Farrington, Jour. of Geol., vol. 9, pp. 405-407 and 525-526.

<sup>&</sup>lt;sup>2</sup> Daubrée, Études Synthétiques de Géologie Expérimentale, t. 1, pp. 236–246.

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magmas in the interior, whether actually combined as water, or as its elements held in solution, or chemically united in other compounds. These gaseous elements form an integral part in the magmas, having been vital factors in their development from the primitive planetary matter. That this process of reworking has gone on to considerable depths, if we are to start with typical meteoritic material, is evidenced by the fact that the deep-seated plutonic rocks are characterized by micas and other hydrous minerals, while mineral species of the meteoritic type are absent.1

The more restrictive phase of the problem of water will be discussed

under the head of vulcanism.

#### VULCANISM.

In the actual dynamics of vulcanism, provided the gases are original in the magmas, the state in which they occur is not of vital importance, except in so far as it determines the conditions under which the gases become free, from occluded or chemical bonds, to perform their part in the mobility of lavas, in the explosions which sometimes accompany eruptions, and in the phenomena of fumaroles and volcanic vents. The distinction between cavity, occluded, and chemically united gas, which is made in the case of solid igneous rocks, can not be extended to the liquid In the liquid lava the gas may be supposed to be imprisoned lavas. mechanically, or else to form a part of the magmatic solution. solidification of the mass, the gas, formerly existing in the free state, may enter chemical combinations at the lower temperature, may be occluded by the solid rock, or may become entrapped within the minerals last to crystallize. So, too, it is possible that some of the gas dissolved in the magma may, because of cooling and crystallization of adjacent portions of the solution, reach a supersaturated condition and appear in the solid rock also as gas inclusions. Otherwise, it would pass into the solid rock occluded or chemically combined. The condition of the gases examined in the laboratory need not, necessarily, correspond to a particular state of occurrence in the lava before crystallization.

Gases mechanically distributed throughout the lava would always be an operative factor in vulcanism, while such gases as were chemically combined in the solution would, presumably, only become free, and hence fully operative, upon the lowering of the temperature and the relief of pressure,<sup>2</sup> and probably but partially then. Since vapors and gases in the free state are the cause of volcanic explosions, they can be traced as far. down in the conduits as explosions occur. From the nature of these explosions, which appear to be due to the accumulation of vapor gradually working upward until suddenly able to relieve itself, it is fair to suppose that

<sup>&</sup>lt;sup>1</sup> This statement should perhaps be qualified. The basalt at Ovifak, Greenland, contains iron strongly resembling the meteoric metal, and in which the minerals cohenite, lawrencite, and doubtfully schreibersite have been recognized. The occurrence of this terrestrial iron would indicate that material of this sort still occurs at points within the outer part of the earth.

<sup>2</sup> A falling temperature favors the liberation of hydrogen from water by ferrous compounds (see p. 67), while carbonates are most easily decomposed at low pressures (see p. 49).

aqueous vapor and the auxiliary gases are present in the free state at still greater depths.

It has been the observation of those who have studied volcanic eruptions that water-vapor is by far the most abundant of the gaseous products of volcanoes. Water is also the principal compound of the element hydrogen, which is quantitatively the most important gas obtained by heating igneous rocks in vacuo. According to one of the common theories of vulcanism, it is water, circulating underground and necessarily dissolving and absorbing mineral and gaseous material, which penetrates to the lavas and gives to them their supply of vapor and gases. Water, then, is a critical element in the theories of vulcanism, and likely to be a decisive factor, upon the basis of which many of these theories may stand or fall. It is, therefore, of great importance to know whether the aqueous vapor, which is so copiously exhaled from volcanic vents and plays such a rôle in vulcanism, is derived originally from the magmas, or is merely underground water which has been incorporated by the lava in its journey upward. decision of this question will carry with it the solution of the allied question concerning the ultimate source of the other gases, and also throw much light upon some of the more comprehensive theories of vulcanism.

Appealing to the fact that chlorine, in the form of hydrochloric acid and volatilized chlorides, is one of the products of volcanoes, one of the standard hypotheses attributes the cause of vulcanism to the penetration of sea-water to the heated interior. If this were so, isolated volcanoes far out at sea would be expected to yield much more chlorine than those on the continents. But the Hawaiian volcanoes exhale comparatively little chlorine or sublimed chlorides. It has been claimed that rain-water, sinking into the cone, would have sufficient head to exclude the sea-water from the neighborhood of the hot lava. Rain, however, falls upon but a small part of the whole cone, whose greater portion is under the sea. It would seem that if rain-water, falling upon a cone built up from the ocean bottom, is able, by means of its head, to keep out the sea-water which covers the lower slopes, the same amount of water precipitated upon a continental volcano would be even more efficient in preventing the general underground water from coming in contact with the lava in the conduit. Whatever may be the reason for the small amount of chlorine given off by the volcanoes of Hawaii, sea-water does not reach the heated lavas in sufficient quantities to affect them appreciably.

On account of the pressure exceeding the crushing strength of the rock, pores and crevices can not exist at depths greater than 30,000 feet according to the most generous estimate, and it is probable that continuous cracks cease much short of this. Beyond this extreme figure, meteoric waters can not be regarded as of any quantitative importance, on account of the extreme slowness of diffusion through solid bodies not containing minute fractures. Liquid carbon dioxide still existing under great pressure in sand grains of Pre-Cambrian age is a concrete example of this slowness. While, theoretically, water may extend downward to the limit of the zone of fracture, the testimony of deep mining appears to show that

<sup>&</sup>lt;sup>1</sup> Hoskins, 16th Ann. Rept. U. S. Geol. Surv., p. 853.

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meteoric waters grow relatively scant, as a rule, below the uppermost 1,500 to 1,800 feet of the earth's crust.¹ This shallowness of meteoric water increases the difficulties encountered by the hypothesis that the lava beds are supplied from this source, since they rise from far greater depths and only the upper portions of their conduits would be exposed to these waters.

It is in this portion of the zone of fracture that Daubrée's much quoted experiment upon the Strasbourg sandstone <sup>2</sup> finds its application, if anywhere, since numerous capillary pores with plenty of water are requisites for the operation of this principle. This famous experiment demonstrated that, owing to its force of capillarity, boiling water will pass through a disk of sandstone, <sup>2</sup> centimeters in thickness, against a slight steam-pressure on the other side. But it was only necessary for the steam-pressure to reach 685 millimeters, or nine-tenths of an atmosphere, in order to prevent any more water from passing through the sandstone. It is a long jump from this trivial capillary force, equal to less than one atmosphere of steam-pressure, to the great pressures which would have to be overcome in the depths of the earth's crust in order to reach the hot lavas, even though it be allowed that the water-vapor, if it came in contact with the lava, would be absorbed. Capillary force seems quantitatively inadequate.

To reach the critical pressure of water due to the hydrostatic column, it is necessary to penetrate the earth to a depth of about 6,900 feet. At depths less than this, water passing into the vaporous condition, in the neighborhood of hot volcanic conduits, at temperatures below the critical point, should leave behind more or less of the matter held by it in solution, since the condensation, and hence molecular attraction of the vapor for solutes, is less than that of the water. Thus even if vapor from underground waters should enter the lavas, as Daubrée has suggested, in the outer 6,900 feet of the earth's crust, much of the chlorides, sulphates, carbonates, and silicates, dissolved in the water, would have been left behind. At depths between 6,900 feet and 25,000 feet, beyond which water can not penetrate, owing to the closure of all pores by the pressure of superincumbent rock, mineral matter dissolved in the water would probably still remain in solution when the liquid passed into the gaseous state at the critical temperature, since the density of the gas is equal to, or greater than, that of the liquid.

The lava, being under considerable pressure, may be supposed to occupy all the cracks and crevices in the adjacent rocks, except those of capillary dimensions. If, therefore, in the passage of underground water into vapor, preparatory to entering lavas in the outer 6,900 feet of the earth's crust, much of the dissolved mineral matter be deposited in the minute pores leading to the lava, they should quickly become sealed, preventing any further access, even of water, to the lava. To test this principle experimentally, a cylinder of medium-grained Potsdam sandstone from Wisconsin, 40 millimeters in diameter and 28 millimeters in thickness, was soldered into a short piece of iron piping, fitted at one end with an elbow

 <sup>&</sup>lt;sup>1</sup> Kemp, Economic Geol., vol. 2 (1907), p. 3; Finch, Proc. Col. Sci. Soc., vol. 7 (1904), pp. 193-252.
 <sup>2</sup> Daubrée, Études Synthétiques, t. 1, pp. 236-246.

to serve as a receptacle for water, and at the other with a cork and a condenser. When ready, the receptacle was filled with Lake Michigan water and a Bunsen burner was placed so as to heat the sandstone cylinder within the iron tube. One side of the sandstone was thus kept at a temperature slightly above 100°, while the other face, in contact with the water, remained just at the boiling-point. Water was found to penetrate the porous cylinder readily, evaporating and leaving its dissolved material within the mass of the sandstone, and escaping as steam on the farther side. The rate at which the water passed through the sandstone at the outset was not determined, but after 5 liters of lake water had been used, it was found that 129 cubic centimeters traversed the rock and were condensed in one hour. The rate slowly fell as the experiment progressed. While the thirteenth liter was being used, only 73 cubic centimeters passed through the sandstone per hour. It was evident that the pores were becoming clogged, but to complete the experiment with Lake Michigan water, which contains only 150 parts of solid matter per million, would have required too much To hasten the process, a saturated solution of calcium sulphate was substituted. This soon caused a marked slackening of the passage of water through the rock, and doubtless would have sealed the pores completely, if allowed sufficient time.

From this experiment, it appears certain that water, evaporating in the pore spaces of a rock and escaping as steam, will leave behind whatever material is in solution, until the crevices become clogged and the penetration of water ceases. This principle may be applied to the outer 6,900 feet of the earth's crust; in the superficial portion of this zone it should be very effective, since the conditions more nearly approach those of the experiment; in the lower portion of this belt, as 6,900 feet and the critical pressure (as well as temperature in the neighborhood of hot volcanic pipes) is approached, the density, and hence the solvent powers, of the water-vapor approach those of the liquid. The vapor, also, should escape less readily from the liquid at these depths, since the expansive force of the vapor drives the water back along its path with more difficulty. Toward the critical point of water, therefore, the application of this principle becomes more uncertain, but it would seem to be operative also at these depths, though more and more slowly as the critical point is neared.

It might be objected that the passage of water into vapor, involving the latent heat of steam, would keep the adjacent rocks cool and cause the deposition to take place at the very contact where the hot lava could fuse, and dissolve, the precipitated salts. But it is very doubtful whether the vaporization of such a small quantity of water, taking place with the slowness imposed upon it by the minuteness of the capillary pores, would keep the contact rocks at a temperature below 365°. The gap between 365° and 1100° is too great for there not to be a space, if of a few inches only, at an intermediate temperature. It is also to be remembered that the latent heat of steam diminishes with the pressure until, at the critical point, it becomes zero. The testimony of the country rocks through which a volcanic conduit has passed is that metamorphism has usually progressed to some distance from the contact of igneous intrusion. In a long-established volcano, where the rocks surrounding the conduit have

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been heated to high temperatures, the deposition of the solutes from any penetrating water should have sealed the capillary tubes and fissures at a distance from the lava such that the latter cannot absorb them and keep the water-way open. Kemp has stated in a recent paper 1 that at the contacts with eruptives, limestone rocks, instead of being porous, are prevailingly dense and compact, and often very hard to drill, as if due to deposition within their interstices. However, the author assigned this supposed deposition to magmatic waters from the intrusion. This brings up a widely established view that magmas, instead of absorbing water from the intruded rocks, give it off, depositing matter in solution to form veins in the sone of fracture.

To quote Van Hise:2

In the belt of cementation, in consequence of the porosity of that zone, the material of the magma, both by direct injection and by transmission through water, may profoundly affect the average chemical composition of the intruded rock for great distances from the intrusive mass.

Geikie cites a case in Bohemia, where certain Senonian marls, invaded by a mass of Tertiary dolerite, begin to get darker in color and harder in texture at a distance of 800 meters from the contact, while, as the intrusive mass is approached, the interstratified beds of sandstone have been indurated to the compactness of quartzite.

But considering only meteoric waters at depths greater than 6,900 feet, where water remains liquid up to the critical temperature, it is less probable that the pore spaces will be filled up in this manner. Nor does it seem likely that Daubrée's theory that water may penetrate rocks against a steam-pressure can operate at these depths, since that principle is dependent upon a marked difference between the capillarity of water and of steam, while at the critical point, the density of water-gas being the same as that of water, this force should be absent. The problem then becomes a question of equilibrium between the hydrostatic column of water and that of the lava, in which the pressure of the lava at a depth of 7,000 feet should be in the neighborhood of 2.7 times that of the water, though this preponderance steadily diminishes as the water-gas becomes condensed, with increasing depth, at a rate higher than lava. Whether under these conditions lava can absorb water-gas, is an open question.

Water can only penetrate from 25,000 to 30,000 feet below the surface on account of the closure of all crevices by pressure. But on the assumption that the temperature gradient in the outer part of the earth's crust is 1° C. for each 100 feet of descent (which is probably too high) the critical temperature will not be reached, except in the neighborhood of volcanic intrusions, until at a depth of about 36,000 feet. Hence, over the greater part of the earth, water will remain in the liquid state as far down as fractures and fissures will allow it to seep, and no appeal can be made to the more rapid and potent gaseous diffusion to carry it beyond 30,000 feet. But because of their heat, lavas must originate at much greater depths below the surface, and hence far beyond the reach of surface-waters, which can

Kemp, Economic Geol., vol. 2, p. 11.
 Van Hise, Monograph 47, U. S. G. S., p. 714.
 Hibsch, cited by Geikie, Textbook of Geology, vol. 2, p. 774.

only come in contact with them, and only doubtfully then, in a very limited portion of the throat of the volcano.

These considerations seem to indicate that, for the most part, the volcanic gases and vapors have not been supplied to the lavas by ground waters, but are original constituents of the magmas. Doubtless at the beginning of an eruption, following a period of quiescence, much of the steam merely comes from such rain-water as may have accumulated in the crater and upper part of the cone, but this does not account for the gaseous emanations from the lava itself, nor from those volcanoes, such as Stromboli, and the well-known Solfatara near Naples, which maintain a mild form of eruption for long periods. Such meteoric water could contribute to the volcanic gases little except some dissolved air, together with a trace of carbon dioxide, and perhaps hydrogen from chemical action. Such soluble salts as this water might dissolve from the crater walls were brought up from the interior in the first place (making some allowance, however, for weathering), and so have little bearing on the case.

The hypothesis that the gases and vapors are originally from the magmas, is greatly strengthened by the volcanic activity in the moon, if, as is rather generally believed, the great pits on the surface of the moon are craters produced by volcanic explosions; if not, of course the argument does not hold. The gases and vapors which caused the tremendous outbursts can not be ascribed to the penetration of surface-waters and gases, for the moon has neither appreciable atmosphere nor hydrosphere, and, according to Stoney's doctrine, never could have held either, owing to its feeble gravitative control. Such gases as are implied by these explosions must be supposed to have arisen from within the interior of the moon. The extent of this explosive lunar vulcanism, in the absence of any appreciable atmosphere or hydrosphere, furnishes a strong argument against the belief that surface-waters and atmospheric gases are essential factors in terrestrial vulcanism.

Thus far evidence of a negative nature has been brought forward to show the difficulties in the way of thinking that surface-waters play a prominent rôle in volcanic phenomena. But more positive evidence can be presented to support the view that the hydrogen and water in the deepseated rocks are truly magmatic. Micas are prominent constituents of the The immense granitic bathyliths, which were probably plutonic rocks. formed beyond the reach of ground-waters, are characterized by this group of minerals. In fact, micas are more abundant in the deep-seated rocks than in the surface lavas of similar composition. Yet all micas contain hydrogen (or hydroxyl) and yield water upon ignition. This varies with the mineral species and locality, ranging up to 4 or 5 per cent. If these micas in the massive intrusions are primary minerals, as they seem to be, and were out of the reach of ground-waters until long after they were crystallized, there appears no other alternative than to consider this hydrogen as inherent in the magma itself. The general petrological principle that plutonic rocks are micaceous and hornblendic, while their more superficial equivalents are more frequently characterized by pyroxenes which are less hydrous, may point toward the suggestion that the magmas originally contain considerable water or the elements which can produce it, but as

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they approach the surface much of the hydrogen and water-vapor escapes and pyroxene minerals crystallize instead of these hydrous micas.

All of these facts and deductions lead to the general conclusion that our surface-waters have been derived from the interior of the earth, and oppose the idea that to explain the presence of hydrogen, or water, in magmas and rocks, we have merely to appeal to the penetration of surface-waters. The meteoric waters are limited to their superficial place and function, both in the evolution of magmas and in vulcanism; an ultimate source is found for these waters; and a steady supply of water and gases is furnished to the earth to offset the loss of vapor into space, and thus contributes to the globe one of the factors necessary to a long period of habitability for living organisms.

#### VOLCANIC GASES.

The gases which escape from fumarolic vents are in many respects similar to those obtained by heating igneous rocks in vacuo, but with the addition of oxygen and vapors of chlorides, fluorides, boric acid, and other high-temperature volatilizations. Though nitrogen is much more conspicuous in the analyses of volcanic gases than in those from rocks, this is doubtless due, in the main, to a mixture with atmospheric air. However, the greater heat of the volcano would also favor a higher proportion of nitrogen, as shown by my experiment. Much of the oxygen also is probably from the air. But an analysis of gas escaping from a stream of lava flowing on the sea bottom at Santorin gave Fouqué: oxygen, 21.11 per cent; nitrogen, 21.90 per cent; and hydrogen, 56.70 per cent.¹ This would suggest that the dissociation of water also contributes free oxygen.

Fouque's studies at Santorin confirm the law of variation in composition of volcanic gases, first established by Sainte-Claire Deville, 2 namely, that the nature of the gas evolved depends upon the phase of volcanic activity. Hydrochloric acid, with free chlorine and fluorine, is given off only from the hottest fumaroles where the heat is sufficient to liberate these gases from chlorides and fluorides. At less active vents, sulphur dioxide is the most noticeable of the corrosive gases, while the cooler fumaroles exhale chiefly hydrogen sulphide, carbon dioxide, and nitrogen. Carbon dioxide and nitrogen escape from all the fumaroles. Fougué found that the relative importance of hydrogen increased with rise of temperature, and that his marsh-gas (which, owing to an imperfection in the method of analysis in 1867, may have been carbon monoxide, or a mixture of carbon monoxide and marsh-gas) diminished as the activity increased. These observations are entirely in accord with the results of my differential temperature experiments with rock powders. Hydrogen sulphide and carbon dioxide are the gases expelled from the rocks at the lowest temperatures; carbon monoxide and marsh-gas appear at intermediate temperatures, while hydrogen is most prominent when the heat is carried to bright redness. Nitrogen is most abundantly liberated at red heat; hence the presence of that gas at the cooler vents and fissures is chiefly due to atmospheric air.

Fouqué, Santorin et ses Éruptions, p. 230.
 Sainte-Claire Deville, Ann. de Chim. et Phys., 52 (1858), p. 60.

While carbon dioxide escapes from all fumaroles in greater or less degree, it is at those vents whose activity has subsided beyond the point where hydrogen and the noxious gases are evolved that this gas is most conspicuous. For this reason, carbon dioxide has come to be regarded as marking the dying of the volcanic activity. A source for carbon dioxide after the disappearance of the other gases has been sought in the neighboring limestone formations, either from baking or from the chemical action of halogen or sulphur acids. The obvious difficulty confronting this conception is that limestone is not always present to furnish carbon dioxide. Experiments show that below 400° C. carbon dioxide is the principal gas evolved from rock material, and as the lava solidifying in the crater, or conduit, has not lost all its gas, it is only a part of the natural sequence of events that the escape of carbonic anhydride from the cooling lavas should continue for some time after the volcano has settled into quiescence. Some of this carbon dioxide doubtless also comes from previous lavas which, warmed again by the fresh lava, give up some of the carbon dioxide which my experiments show them to contain.

#### AMMONIUM CHLORIDE DEPOSITS.

Among the various substances which are deposited around fumaroles, sal-ammoniac, or ammonium chloride, is, in some respects, one of the most remarkable. Compounds of ammonium have not yet been recognized in igneous rocks, although rock powders often give off small quantities of ammonia gas when heated in vacuo. Chemical analyses of spring-waters report ammonium salts only in traces, such as may have been derived from the decay of organic matter. If ground-waters be, for the most part, unable to reach the lavas, even this rather doubtful source of ammonium compounds is not available. If the elements of the radical NH, be supposed to have come from the interior magma, there are two alternative hypotheses still open. The first assumes that the radical NH4 existed intact in the magmatic solution in the form of ammonium salts and, volatilized by the heat upon the relief of pressure, gradually collected on the cooler portions of the crater. This hypothesis must, however, explain the apparent absence of these compounds in igneous rocks. The second believes that the ammonium chloride was formed synthetically in the throat of the volcano, from the nitrogen, hydrogen, and hydrochloric-acid gases. This would make it a direct product of volcanic gases.

The presence of ammonia, or its vaporized salts, in volcanic emanations leads to the formation of another interesting compound. Silvestri has found iron nitride, as a lustrous metallic deposit, at a fumarole on Etna. This compound is due either to a reaction between the sublimed ferric chloride and free ammonia gas or to the ignition of the iron-bearing lava in the presence of ammonium chloride vapor. The appearance of iron nitride around fumaroles throws no direct light upon the question of its existence in the magmas, though it indirectly leads to the hypothesis that the nitrogen in the ammonia and its compounds came originally from iron nitride within the magma.

<sup>&</sup>lt;sup>1</sup> Silvestri, Pogg. Ann., vol. 157 (1876), pp. 165-172.

#### SUBTERRANEAN GASES.

The atmosphere is now being fed by gases which escape through outlets other than those of active volcanoes. Work in the shafts of many deep mines in different parts of the world is often impeded by the exhalation of gases from the rocks. This is, of course, familiar in the case of organic rocks, such as coal, in which the decomposition of organic substances is in progress. Reference is here made especially to gases escaping from crystalline or other inorganic rocks. An exhalation of this kind is a notable phenomenon in several of the mines in the Cripple Creek region of Colorado, where nitrogen and carbon dioxide are poured into the workings in considerable quantities when the barometer is low. Two analyses of the gas escaping into the Conundrum mine at Cripple Creek gave the following:

1st: Carbon dioxide, 10.2; oxygen, 5.7; nitrogen, 84.1; total, 100. 2d: Carbon dioxide, 8.3; oxygen, 10.2; nitrogen, 81.5; total, 100. No carbon monoxide, marsh-gas, or hydrocarbons were detected.

The gas from the Elkton mine, which was analyzed by Dr. A. W. Browne, of Cornell University, consisted of nearly the same gases as from the Conundrum mine: Water-vapor, 1.4; carbon dioxide, 14.7; oxygen, 5.6; nitrogen, 76.8; argon, 1.5; total, 100.0. Hydrocarbons, methane, and hydrogen were absent.<sup>2</sup> The authors estimate that this gas may be considered to be 25 per cent of air, 59 per cent of nitrogen and argon, 15 per cent of carbon dioxide, and 1 per cent of water-vapor. The gas apparently is derived from greater depths than those at which it issues, since it is warmer than the air of the mines, and since practically no gas was encountered in the oxidized zone. They regard the outpouring as the last exhalation of the extinct volcano, around whose neck the Cripple Creek mines are located.

In some of the potash mines in the vicinity of Strassfurt trouble is caused by the escape of combustible gas into the workings. According to Precht, blowers of this gas once lighted have burned continuously for periods as long as two months. An analysis of this gas by Precht shows it to be largely hydrogen. His figures are: Hydrogen, 93.05; methane, 0.778; carbon dioxide, 0.180; carbon monoxide, trace; oxygen, 0.185; nitrogen, 5.804; total, 100.002. This investigator believed that but little of the hydrogen could have come from the decomposition of organic matter; instead, he sought a source for it in the possible oxidation of ferrous chloride in the salt by water, according to the reaction:

$$6 \text{FeCl}_2 + 3 \text{H}_2 \text{O} = 2 \text{Fe}_2 \text{Cl}_6 + \text{Fe}_2 \text{O}_2 + 3 \text{H}_2$$

This source of hydrogen is somewhat analogous to the production of the same gas by the action of water upon ferrous compounds at high temperatures, which has already been discussed, except that in the salt beds the supposed action has taken place at the ordinary underground temperature. But these gases coming from the sedimentary salt beds of the Upper Permian represent, of course, gas merely restored to the atmosphere, and not an original contribution to it.

<sup>&</sup>lt;sup>1</sup> Lindgren and Ransome, Prof. Paper 54, U. S. G. S., pp. 252–270.

<sup>2</sup> H. Precht, Ber. Deutsch. Chem. Gesell., vol. 12 (1879), pp. 557–561.

Nitrogen with an abnormal amount of inert gas (probably both argon and helium) occurs, under high pressure, in a gas-well at Dexter, Kansas.¹ However, instead of being derived from igneous rocks, this comes from a gas-bearing sand near the contact of the Permian with the Upper Carboniferous. An analysis of this gas gave:² Oxygen, 0.20; methane, 15.02; hydrogen, 0.80; nitrogen, 71.89; inert residue, 12.09; total, 100.

Neither carbon dioxide nor carbon monoxide was present in this gas. The methane, and perhaps the hydrogen also, may be attributed to the decomposition of organic matter, since natural gas-wells exist at no great distance away. But the remarkable feature of this analysis is the large amount of nitrogen with the very abnormal percentage of inert gas. From this analysis, and the testimony of many spring-waters which give off considerable quantities of argon and helium, it would appear that gases often collect underground somewhat in proportion to their chemical inertness. The chemically active gases apparently are more largely retained within the rocks by combination, while nitrogen, having less power to unite chemically, more largely escapes from the rocks and accumulates in reservoirs. Argon, still more inert than nitrogen, thus may reach such a high proportion as 12 per cent.

#### GENERAL RELATIONS.

#### RELATIVE TO THE HYPOTHESIS OF A MOLTEN EARTH.

These studies show that, within the range of temperature employed, heat causes the expulsion of gases in whatever form they are held, and that the greater the degree of heat the more quickly and completely the gases are given off. There is reason to believe that this principle applies to the molten state as well as to the solid condition. If it be applicable to liquid lavas, it would favor the belief that a molten globe would have boiled out most of its gaseous matter before solidifying. Gases near the surface should escape rapidly. It might, perhaps, on first thought, be held that, while much of the gas in the outer portion would be lost, that existing in the central part of the sphere would be retained and slowly recharge the peripheral portion after a crust had formed and prevented further escape; but the molten globe, by hypothesis, grew up gradually, and essentially every part was once superficial. Even to-day, in an essentially solid earth, there are movements of lava that bring up gases from unknown depths, and it is reasonable to suppose that the molten sphere was stirred up by still more effective convection currents which facilitated the expulsion of gases and vapors, and that almost all of the gaseous material of the globe would have been boiled out before solidification set in.

The complete validity of this view depends much upon the fate of the gases after they have reached the surface. If they were retained in the form of a dense atmosphere, a condition of pressure-equilibrium might be established between the atmosphere and the gases in the liquid earth, by means of which the latter would retain some appreciable amount of gas. But if, as some believe, our atmosphere is about all that the earth

<sup>&</sup>lt;sup>1</sup> Haworth and McFarland, Science, vol. 21 (1905), pp. 191-193. 

<sup>2</sup> Loc. cit.

can control, the gas expelled from the molten sphere in excess of the mass of the present atmosphere would escape and be lost to the planet. Geological evidences—early Cambrian glaciation, Paleozoic periods of aridity, and the general testimony of life—all point toward the conclusion that early terrestrial atmospheric conditions were not radically different from those of to-day. If the hypothesis of a heavy atmosphere be not permissible, it becomes very difficult to explain the presence of original gases and gas-producing compounds in plutonic rocks on the basis of the Laplacian or other hypotheses that postulate original fluidity.

#### RELATIVE TO THE PLANETESIMAL HYPOTHESIS.

After the gaseous matter of the ancestral sun was shot out from the solar surface to form the two arms of the spiral nebula, as postulated by the planetesimal hypothesis, the rock-producing portion is supposed either to have aggregated into planetesimal bodies, or to have been gathered, molecule by molecule, into the nucleus of the earth. The planetesimal bodies gathered in gas molecules of the atmospheric class both by chemical union and by surface adhesion or occlusion. As the earth grew by sweeping in the planetesimals, whatever gases they contained became entrapped in the body of the growing planet and well distributed throughout its mass. At first, the gravity of the earth may possibly have been able to hold only the gases brought in by planetesimal aggregates of rock material and those that became impounded in it by impact, but at a later stage, when increased mass enabled it to hold gaseous molecules, gases may have been added to the atmosphere directly from the nebula, and these, by chemical reactions, may have become united with the surface rocks. soon as vulcanism commenced, a system of exchange was set up. gases were being fed to the atmosphere by volcanic action, water, carbon dioxide, oxygen, and nitrogen were being buried with the surface rock material, partly by chemical union and partly by mechanical entrapment, as the growth by infalling matter continued. It is thus quite easy to understand how the earth came to be affected by these gases throughout its mass, and how they came to exist there in all available forms of retention.

While the carbon monoxide and methane derived from rocks by heating in vacuo are doubtless chiefly produced from the carbon dioxide and water present in the rock material, there seems good reason to suppose that similar reactions took place within the earth, as the surface material became buried and heated, and hence that carbon monoxide and methane exist, as such, in the earth's body, and are to be reckoned among the natural gases of the rocks.

#### RELATIVE TO ATMOSPHERIC SUPPLY.

The fact that many of the igneous rocks are able to yield hydrogen from reactions between water and ferrous compounds, at high temperatures, indicates that the material of the earth's crust is in a condition of partial oxidation only. Near the center of the earth there is probably very little oxygen, and even up to the surface, barring the weathered

<sup>&</sup>lt;sup>1</sup> R. H. McKee, Science, vol. 23 (1906), pp. 271-274.

mantle, the rocks are suboxidized. Yet the earth is surrounded by an oxygenated atmosphere. Since oxygen is not developed in the combustion-tube, and does not appear to exist as a free gas in igneous rocks, it is not likely that this constituent of the atmosphere has come directly as an exudation from the interior of the globe. It is to be sought, rather, in a dissociation or decomposition of compound gases by physical or organic agencies. Originally, enough oxygen was derived from water-vapor, by physical means, to permit the beginning of plant life; after vegetation appeared, an abundant source of oxygen was found in the carbon dioxide.

The average gas content of igneous rocks, as determined by the analyses now made, may be used to test the competence of the rocks to yield the present atmosphere. Taking the average volume of nitrogen per volume of rock to be 0.05, which is probably nearer the truth than the figure 0.09 given in table 16 ¹ (owing to leakage of air), it would require the liberation of all the nitrogen in the outermost 70 miles of the earth's crust to produce the nitrogen in the present atmosphere. For an estimate of the amount of igneous rock necessary to yield the carbon dioxide which is now locked up in limestone and coal deposits, we may take Dana's figure of 50 atmospheres of this gas, and an average of 2.16 volumes of carbon dioxide per volume of rock. To produce these 50 atmospheres of carbon dioxide, it is found that a thickness of 66 miles of crust would have to be deprived of its carbon dioxide ²—a figure which corresponds fairly well with the estimate for nitrogen. If the water of the rocks be placed at 2.3 per cent, a depth of 70 miles would supply the hydrosphere.

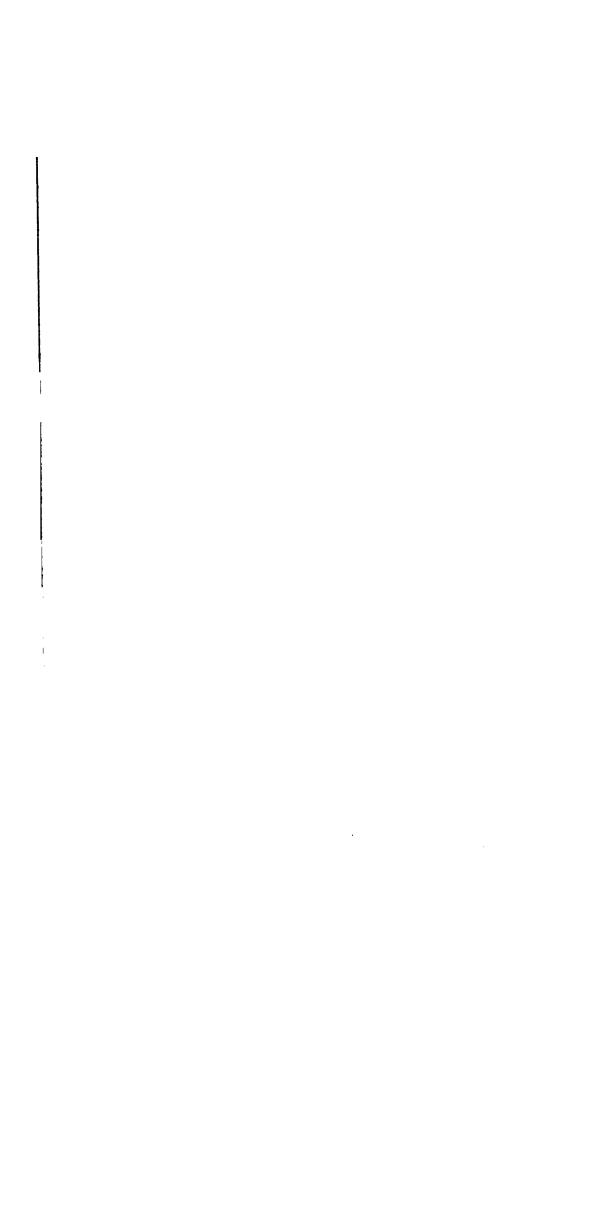
On the planetesimal hypothesis, gas has been supplied from the interior to the atmosphere ever since an early stage of the earth's growth, probably from the earliest stage at which an atmosphere could be held, which may be placed at the time when the earth's radius was about 2,000 miles. From this it appears that only a small fraction of the full gas-producing possibilities of the rocks of the earth was required to supply the atmosphere. The fact that gases are still being given forth through volcanoes, and that the ejected lavas still have gas-producing qualities, makes it clear that all the resources of the interior are not yet exhausted. The working qualities of the planetesimal hypothesis, therefore, do not seem to be found wanting in either past possibilities of supply, present output, or prospective reserve.

#### ACKNOWLEDGMENTS.

In conclusion, I wish to express my special thanks to Dr. Julius Stieglitz for constant advice in the conduct of the chemical researches; to Dr. Oskar Eckstein for much valuable assistance in the laboratory; to Dr. R. A. Millikan for helpful suggestions pertaining to physical principles and the designing of new pieces of apparatus; and to my father, Dr. T. C. Chamberlin, for proposing the investigation, and for constant sympathy and criticism during the progress of the work.

<sup>&</sup>lt;sup>2</sup> Ante, p. 28. <sup>3</sup> The limestones, of course, are not here included.





#### CONTRIBUTIONS TO COSMOGONY AND THE FUNDAMENTAL PROBLEMS OF GEOLOGY

### THE TIDAL AND OTHER PROBLEMS

BY

T. C. CHAMBERLIN, F. R. MOULTON, C. S. SLICHTER, W. D. MACMILLAN, ARTHUR C. LUNN, AND JULIUS STIEGLITZ.



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#### I. THE TIDAL PROBLEM.

THE FORMER RATES OF THE EARTH'S ROTATION AND THEIR
BEARINGS ON ITS DEFORMATION. By T. C. CHAMBERLIN.

THE ROTATION-PERIOD OF A HETEROGENEOUS SPHEROID.

BY C. S. SLICHTER.

ON THE LOSS OF ENERGY BY FRICTION OF THE TIDES.

By W. D. MACMILLAN.

ON CERTAIN RELATIONS AMONG THE POSSIBLE CHANGES IN THE MOTIONS OF MUTUALLY ATTRACTING SPHERES WHEN DISTURBED BY TIDAL INTERACTIONS. By F. R. MOULTON.

Notes on the Possibility of Fission of a Contracting Rotating Fluid Mass. By F. R. Moulton.

THE BEARING OF MOLECULAR ACTIVITY ON SPONTANEOUS
FISSION IN GASEOUS SPHEROIDS.

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П.	GEOPHYSICAL	THEORY	UNDER	THE	PLANETESIMAL	HYPOTHESIS.	
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By Julius Stieglitz.

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CONTRIBUTIONS TO COSMOGONY	AND THE FIND.	AMENTAI. PROBLEMS	LUK GEULUGA

# THE FORMER RATES OF THE EARTH'S ROTATION AND THEIR BEARINGS ON ITS DEFORMATION

BY
THOMAS CHROWDER CHAMBERLIN
Professor of Geology, University of Chicago

•		

## THE FORMER RATES OF THE EARTH'S ROTATION AND THEIR BEARINGS ON ITS DEFORMATION.

In the treatment of the earth's deformations, which is to be the subject of a following paper, it is essential to know whether changes in the rate of the earth's rotation must be regarded as one of the important factors or not. If the rate of rotation has appreciably varied during geological history, it is almost certain that the oblateness of the earth-spheroid has also varied, for unless the rigidity of the earth greatly exceeds that of any known substance, it must have been modified in form under changing rotation so as to approach the shape it would assume if it were a perfect fluid. It would be an error to assume, as is sometimes done, that the earth would conform to the fluidal shape perfectly, but that it would approach to this with a measurable degree of closeness seems to be beyond question. If there was a change from a high rotational speed, and consequent high degree of oblateness, to a slower speed with less oblateness, the surface area of the earth must have been reduced, because the nearer such a body approaches a sphere, the less the area of its surface, the greater its average gravity, and hence the greater its degree of compression. This is brought out numerically, with a high order of approximation, in the accompanying paper of Professor Slichter. There will be occasion in the course of the present paper to consider in detail the application of this supposed reduction.

Whatever therefore may be the difficulties attending a treatment of past rates of rotation of the earth, it is imperative that this element of the problem of deformation be recognized and evaluated so far as lies in

our power.

The problem may be approached on two rather distinct lines, one of which is astronomic but rests back so radically on postulates derived from theories of cosmogony that it may almost be called cosmogonic, and the other of which is geologic and rests on the direct or implied teachings of terrestrial evidence.

The ulterior purpose of this paper is to set forth the latter, but the cosmogonic considerations can not be passed without notice, for the cogency which will be thought to attach to geological evidences is certain to be measured in no small degree by the presumptions which are entertained on cosmogonic grounds, or on astronomic grounds with an essential cosmogonic factor. The recent literature of the subject indicates that a belief in a former high rate of rotation of the earth based on cosmogonic and tidal grounds has a strong hold on astronomers and, to some large

extent, upon geologists. The extent of this belief is due in large measure, no doubt, to the masterly papers of Sir George Darwin upon the origin and tidal influence of the moon. It is obvious that if the arguments in favor of a former high rate of rotation are accepted as decisive in themselves, such geological data as seem to conflict with them are likely to be received with skepticism, or to be given interpretations consistent with the accepted conclusions. It is therefore appropriate, if not necessary, to review at the outset the grounds for the conclusions that have been drawn from cosmogonic postulates and from tidal and other considerations based upon these, so far at least as these have been thought to be weighty. There is the more reason for this in the present series of papers, because of the very different basal postulates which may be grounded on the mode of planetary genesis set forth in them.

#### THE ASTRONOMICAL DEDUCTIONS.

#### CONSIDERATIONS BASED ON THE OLDER COSMOGONIES.

It scarcely needs to be recited that, during the past century, astronomers and geologists almost universally accepted the hypothesis that the earth was formed from the condensation of a spheroid of gas, and that current doctrines as to the earth's early rates of rotation were founded on premises derived from some form of this hypothesis. Under the original Laplacian view it was affirmed that the rotations of the sun and the planetary masses were progressively accelerated as they shrank from a more expanded to a more dense condition. The rotation of the parent earthmoon spheroid was supposed to have reached, at a certain stage, such a velocity that a ring of matter was separated from its equatorial tract and formed the moon by subsequent condensation. It was held that the speed of rotation of the residual spheroid further increased, or tended to increase, by reason of its continued contraction, and hence that the primitive rotation of the earth was exceedingly rapid. As the present rotation of the earth is relatively slow, it followed, as a necessary inference, that a very marked decline in the earth's rotatory velocity took place in the course of geological history.

In the modification of the Laplacian view introduced by Sir George Darwin, the material of the moon is supposed to have been separated

<sup>&</sup>lt;sup>1</sup> G. H. Darwin:

G. H. Darwin:

On the bodily tides of viscous and semi-elastic spheroids, and on the ocean tides upon a yielding nucleus. < Phil. Trans. Roy. Soc. Lond., part 1, 1879, pp. 1-35. On the procession of a viscous spheroid, and on the remote history of the earth. < Phil. Trans. Roy. Soc. Lond., part 2, 1879, pp. 447-538.

Problems connected with the tides of a viscous spheroid. < Phil. Trans. Roy. Soc. Lond., part 2, 1879, pp. 539-593.

The determination of the secular effects of tidal friction by a graphical method. < Proc. Roy. Soc. Lond., No. 197, 1879, pp. 168-181.

On the secular changes in the elements of the orbit of a satellite revolving about a tidally-distorted planet. < Phil. Trans. Roy. Soc. Lond., vol. 171, part 2, pp. 713-891, 1880; Proc. Roy. Soc., vol. 29, 1879, p. 168, and vol. 30, 1880, p. 255.

On the tidal friction of a planet attended by several satellites and on the evolution of the solar system. < Phil. Trans. Roy. Soc. Lond., part 2, 1881, pp. 491-535.

Enc. Brit., article on "tides"; "The Tides." 1899.

Also Thomson and Tait's Natural Philosophy, 2, articles on tides.

Also Thomson and Tait's Natural Philosophy, 2, articles on tides.

from that of the earth after the condensation of the common mass had reached the liquid or perhaps even incipient solid state. In what precise form the separation took place is not specifically affirmed and is not material here, where the only essential point is the high rotatory velocity assigned the earth at the time of the moon's separation.

Most or all of the meteoritic hypotheses of the earth's origin—using the term meteoritic in the restricted sense defined in this series of papers—agree essentially with the gaseous hypotheses in assigning to the earth, at its earliest separate stage, a molten condition and a rate of rotation either identical with or closely approximate to that of the Laplacian hypothesis and of its modifications. The presumption, therefore, that the rotation of the primitive earth was of a high order of velocity had the sanction of these two classes of cosmogonic theories, and, as they occupied the field almost exclusively during the past century, this common inference from them came to have, naturally enough, a strong hold upon the beliefs of astronomers and geologists. If there shall finally be found reason to set these conceptions aside, it should still be recognized that they have been powerful instrumentalities in advancing knowledge and in stimulating inquiry, and that the investigations founded upon them have been scarcely less than necessary steps toward a final solution.

Besides being at one in postulating a rapid rate of primitive rotation, these older hypotheses were essentially in agreement in assigning to the earth a molten condition in its early stages, as already stated, and this postulate has entered pervasively into the tidal and deformative theories of the earth that have had currency. Until the later decades of the last century, it was commonly believed that a molten condition was retained by the interior of the earth, or by some notable part of it, throughout the geological ages. In the latter part of the century, the conception of a solid earth came to be more generally entertained, but there went with this, almost universally, the postulate of such a degree of viscousness as to profoundly influence conclusions relative to tidal deformation and earthmovements generally. At the present time, when belief in an essentially solid earth has gained a large, though not universal, adherence, the conception that the spheroid is to be regarded as a viscous body in the treatment of all the larger geological problems is still widely prevalent and not only enters profoundly into the study of these problems but takes on forms exceedingly difficult to adjudicate. The embarrassment does not arise so much from the theoretical recognition of a viscous property in the substances of the lithosphere, as from the lack of firm grounds for estimating its actual participation in the deformations and internal movements of the earth. One of the most vital questions of earth-dynamics relates to the respective values of viscousness and of elastic rigidity in terrestrial diastrophism.

In this discussion the elastic rigidity of the earth will be regarded as the dominant factor in its morphology, and the tidal deformations of the lithosphere will be regarded merely as strains in an elastic body, involving viscous or liquid flowage only as an incident affecting those portions of the earth's body which are in a molten, gaseous, or temporarily unattached state.

Working upon the cosmogonic grounds prevalent in the past century, and supported by the nearly universal consensus of opinion regarding the early stages of the earth, Sir George Darwin, in a memorable series of mathematical investigations, developed the well-known doctrine of the tidal retardation of the earth's rotation from a primitive period of less than 5 hours 36 minutes to the present period of four times that length. Besides being grounded in presumptions that were commonly accepted, it had the merit of bringing these presumptions into historical consistency with the existing state of things. Not only that, but the investigation started with what then seemed to be a present rate of retardation deduced from astronomical observations, and proceeded backward by logical steps and current assumptions to the supposed original state, or at least to a close approach to it. The confidence that has been reposed in the conclusions so reached has not been placed without persuasive reasons, whatever conclusions may ultimately be reached from radically different cosmogonic postulates and from revised astronomical data.

Not a few inferences of vital geological importance were drawn from this classic investigation, and specific data to support them were naturally sought in the geologic record. For the greater part, this search met with negative results, or with results which could be regarded as giving but meager or equivocal confirmation. Notwithstanding this, the logical force of the tidal argument as developed by Sir George Darwin, when its cosmogonic postulates were taken for granted, was such that inharmonious geological phenomena were generally explained away, largely by assuming that the internal solidification of the earth took place at a relatively late date.

#### CONSIDERATIONS BASED ON THE PLANETESIMAL THEORY.

As to the grounds for postulating a radically different constitution of the lithosphere, growing out of a new hypothesis of earth-genesis, I must content myself here with references to what has already been written 2 and to a fuller exposition elsewhere in this series of papers. It is appropriate, however, to bring again to mind those inferences which are drawn from the rotational features now shown by the solar system, since these bear specifically upon the question in hand.

The doctrine that a prevalent forward rotation of the planets could only mean that they were formed through gaseous or quasi-gaseous condensation, was one of the bulwarks of the older hypotheses. It was only

<sup>&</sup>lt;sup>1</sup> Cit., ante.

Cit., ante.
 A group of hypotheses bearing on climatic changes, T. C. Chamberlin, Jour. Geol., vol. 5, No. 7, 1897, pp. 653-683.
 An attempt to test the nebular hypothesis by the relations of masses and momenta, T. C. Chamberlin, Jour. Geol., vol. 8, No. 1, Jan.-Feb., 1900, pp. 58-73.
 An attempt to test the nebular hypothesis by an appeal to the laws of dynamics, F. R. Moulton, Astrophys. Jour., vol. 6, No. 2, Mar., 1900, pp. 103-130.
 Certain recent attempts to test the nebular hypothesis, T. C. Chamberlin and F. R. Moulton, Science, vol. 12, Aug. 10, 1900.
 The origin of the earth, Chamberlin and Salisbury, chap. I, vol. 2, Geology, pp. 1-81 Dec., 1905.

Dec., 1905.

Evolution of the solar system, F. R. Moulton, chap. XV, Introduction to Astronomy, pp. 440–487, Mar. 24, 1906.

when the inapplicability of this doctrine to natural cases was detected. about a decade ago, that there was a clear path opened and logical grounds provided for developing a hypothesis of planetesimal accretion. perhaps not too much to assume that the previous papers of this series have shown that this hypothesis is even better fitted than gaseous condensation to give rise to the various rates of rotation actually presented by the solar system. Under the planetesimal hypothesis, the primitive rotation of the earth was not necessarily rapid, nor was the body of the earth necessarily molten. Thus two of the primitive conditions, that were formerly taken for granted on the basis of a nearly universal consensus of opinion, have been brought into question and may now be fairly regarded as being at best no more than working competitors with the alternative of a solid elastico-rigid earth, a view which is hampered by no compulsory presumption as to any particular rate of primitive rotation, but is hospitable to any rotational state which the direct evidences, astronomical, geological and otherwise, may require.

The speculative freedom relative to primitive rotations, which the planetesimal hypothesis thus affords, directs attention anew to the actual facts and to their unembarrassed implications. The most fundamental case is that of the controlling body of the solar system itself. The present rotation of the sun is relatively slow and its axis is inclined appreciably to the common plane of the planetary system. When it is considered that the mass of the sun is more than 700 times that of all the planetary derivatives combined, this rate and this inclination assume radical importance. This slow rotation and this inclination of axis are perfectly consistent with the planetesimal hypothesis and have peculiar suggestiveness in that relationship. On the other hand, they seem to me very difficult to reconcile with any theory under which the outlying bodies are supposed to be derived from a gaseous or quasi-gaseous spheroid by contraction, particularly any theory which postulates that the derived bodies were discharged from the central mass by the equatorial velocity of its rotation. Obviously the planetary material thus separated should be accurately adjusted to the sun's equatorial plane, and to the common plane of the system. Obviously also the great residual mass should have a rate of rotation appropriate to such a discharge. Having separated a succession of masses from its equator to form the planets, and having further shortened its radius some 36,000,000 miles after the last known planetary mass was detached, the sun should have a rotatory velocity somewhat near that requisite for another planetary separation. The velocity of rotation at the equator of the solar nebula when it was supposed to have detached the material for Mercury must have been, according to the Laplacian hypothesis, about 28 miles per second. The equatorial velocity requisite to bring the centrifugal and centripetal components of the sun's equatorial motion into equality if the sun now had a radius of 1,000,000 miles is 176 miles per second; the velocity required to bring about this state at the present surface of the sun is 270 miles per second. We should then expect,

<sup>&</sup>lt;sup>1</sup> Journal of Geology, vol. 5, 1897, pp. 668-669

under any hypothesis that rests on centrifugal separation, that the present speed of the sun's equator would certainly be much greater than 38 miles per second, and should approach the higher figures given. As a matter of fact, the sun's equatorial velocity of rotation is only about 1.3 miles per second. Such a rate seems, therefore, to be altogether inconsistent with the doctrine of centrifugal separation. If, for a moment, the thought be entertained that tidal retardation may have reduced the sun's rotation from a high primitive rate consistent with the centrifugal hypothesis, to the present rate, it will become obvious, on a study of the nature and value of the tidal influence of the planets on the sun, that this is wholly untenable. The quantitative estimates of Sir George Darwin are decisive on this point.¹ So also is the remarkable fact that the equatorial portion of the sun has a higher rotational velocity than the portions in higher latitudes instead of lagging, as it should if it were affected by tidal retardation.

The obliquity of the sun's axis is a further grave objection to all forms of the doctrine of centrifugal separation. On the other hand, some such obliquity is extremely probable under the hypothesis that the system was developed by the influence of a passing star, for the axis of the ancestral sun might obviously sustain any relationship to the orbital plane of the disturbing body. The position of the present axis, under this hypothesis, is the result of a composition of moments of momentum derived in part from the ancestral rotation and in part from the passing star, and it could not therefore be expected, except by a remote chance, to be exactly normal to the common plane of the planetary system. Under this hypothesis the obliquity of the sun's axis, together with its slow rotation, suggest, if they do not distinctly imply, that the direction of rotation of the ancestral sun was opposite to that of the present sun, and that its axis was more inclined than now to the plane of the present system.

Of similar rotational import is the relationship between the time of rotation of Mars and that of the revolution of its inner satellite, Phobos. It is obvious that, under any hypothesis of centrifugal separation, if a revolving spheroid acquires by contraction an equatorial velocity sufficient to leave behind the material of a satellite, and afterwards continues to contract until its radius is but a small fraction of its value at the time of separation, the rate of rotation of the spheroid must be greatly increased and its period must be much shorter than the revolutionary period of the derived satellite, unless some very potent agency intervenes to reverse the systematic process of the evolution. Now, the satellite Phobos revolves around Mars about three times while the planet rotates once. In an analogous way the little bodies that make up the inner edge of the inner ring of Saturn revolve about that planet twice while the planet rotates once. These are, on their face at least, seriously out of accord with the doctrine of centrifugal separation by planetary contraction. Darwin has suggested that tidal retardation may be a possible solution in the special case of Phobos, but Moulton has called attention to the insuperable difficulties of applying this explanation consistently to the Saturnian case and the Martian case at the same time.2

<sup>&</sup>lt;sup>1</sup> Trans. Phil. Soc. Lond., 1881. 

<sup>2</sup> Astrophys. Jour., vol. 11, Mar., 1900, p. 109.

The retrograde revolution of the ninth satellite of Saturn still further and seriously complicates the case from the centrifugal point of view.

The rotations of Uranus and Neptune are unknown, but, whether they are concordant with the revolutions of their satellites or not, they present difficulties under the centrifugal hypotheses because of the great obliquity of the planes of revolution of their satellites to the common plane of the system, and because of their retrograde motions. This has long been recognized, but these difficulties gain not a little in force when they are associated with other rotational difficulties which have been insufficiently considered in connection with them.

There are still other rotational features of the existing planets which seem to be inconsistent with all forms of a contractional-centrifugal hypothesis of planetary origin, and, what is especially to the point in the matter in hand, which seem inconsistent with the very high rotational velocities which such a hypothesis necessarily postulates. Among these are the great differences in the rotational features of the members of the system. If the system started from a common spheroid and if its derivatives were shed by systematic centrifugal action, it is very difficult to see how so great variety of rotational velocities, so varied inclinations of the rotational axes, and so diverse directions of rotation as the system actually presents, could have arisen.

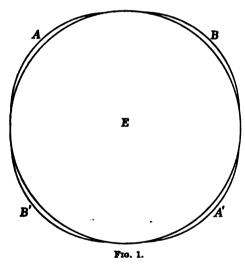
Under the planetesimal hypothesis, the rotation of each planet is held to have arisen independently of every other planet. Its rate of rotation depended on the special conditions that attended the expulsion of its nucleus from the sun, and on the mode of accession of the rest of its material from the planetesimal state—conditions that were quite certain to vary with each planet. Rotations, rapid or slow, direct or retrograde, with inclinations of any degree, are consistent with the hypothesis. There is, however, a decided balance of presumption in favor of forward rotations, of moderate inclinations of axis, and of moderate velocities of rotation. As none of the planets rotate at speeds that even remotely approach that requisite for equatorial discharge, as their rates of rotation differ widely from one another, as the inclinations of their axes vary greatly, and as the majority of their rotations are direct and the minority retrograde, this hypothesis seems to be concordant with the facts of the case.

If we are thus permitted to start with a genesis which leaves us free to suppose that the rate of the earth's rotation at the outset may have been essentially what it is to-day, or may have been faster or slower in any degree, the preconceptions that have led to former rotational views do not trammel us. The determination of the past history of the earth's rotation rests unhampered upon the evidences presented by its own phenomena and upon those deducible from the necessary influence of its neighbors.

The most important of the rotatory influences of neighboring bodies on the earth is the friction of the tides, particularly of the lunar tides. The assigned mode of this action is familiar and may be stated briefly as follows: If the tidal protuberance has a position in advance of the position of the moon, as at A in fig. 1, a component of the moon's attraction tends to antagonize the earth's rotation and to accelerate the moon's motion.

If a tidal protuberance has a position behind the moon's position, as at B, a component of the moon's attraction tends to accelerate the earth's rotation and to retard the moon's motion. If a protuberance rises directly beneath the moon's position, its forward and backward pulls are equal.





On the opposite side of the moon there are complementary protuberances, as A', B', fig. 1, whose rotatory effects are the reverse of those on the moonward side, but whose greater distances give them less efficiency. It is merely this difference in effectiveness growing out of difference of distance that is usually appealed to as influencing rotation.

I shall endeavor to show later that, while the foregoing reasoning seems to be unimpeachable in itself, there are counterbalancing factors which seem to have been overlooked, and which nullify the value of this mode of treatment. They do not, however, nullify the proposition that tidal friction tends to retard the earth's rotation. It seems best, however, to review the subject first on the accepted lines.

The tides represented in fig. 1 are such as are assigned to the direct pull of the tide-producing body and are known as "direct." The protuberance A, fig. 1, represents a tide which is interpreted as having lagged in its formation, and hence has been carried forward by the rotation of the earth to a position in front of the moon's position; B represents a tide which has been formed behind the moon's position, but

behind the moon's position, but both may be regarded as falling within the class of "direct" tides. This class of tides are said to be built up when the natural free period of the tidal wave is less than that of the tidal forces. If the natural free period of the tidal wave is greater than that of the tidal forces, the tendency is to produce "inverted" tides. The law underlying this difference of result, to which Newton first directed attention, is thus stated by Darwin:

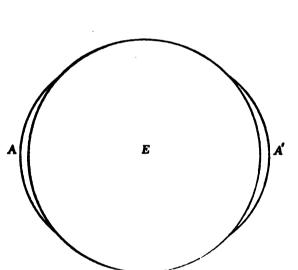
<sup>&</sup>lt;sup>1</sup> The Tides, pp. 171–172.

Now, this simple case illustrates a general dynamical principle, namely, that if a system capable of oscillating with a certain period is acted on by a periodic force, when the period of the force is greater than the natural free period of the system, the oscillations of the system agree with the oscillations of the force; but if the period of the force is less than the natural free period of the system the oscillations are inverted with reference to the force.

This principle may be applied to the case of the tides in the canal. When the canal is more than 13‡ miles deep, the period of the sun's disturbing force is 12 hours and is greater than the natural free period of the oscillation, because a free wave would go more than half round the earth in 12 hours. We conclude, then, that when the tide-generating forces are the tide-generating trying to make it high water, it will be high water. It has been shown that these forces are tending to make high water immediately under the sun and at its antipodes, and there accordingly will the high water be. In this case the tide is said to be direct.

But when the canal is less than 13\(^2\) miles deep, the sun's disturbing force has, as before, a period of 12 hours, but the period of the free wave is more than 12 hours, because a free wave would take more than 12 hours to get half round the earth. Thus the general principle shows that where the forces are trying to make high water, there will be low water, and vice versa. Here, then, there will be low water under the sun and at its antipodes, and such a tide its said to be inverted, because the oscillation is the exact inversion of what would be naturally expected.

All the oceans on the earth are very much shallower than fourteen miles, and so, at least near the equator, the tides ought to be inverted. The conclusion of



F10. 2.

the equilibrium theory will therefore be the exact opposite of the truth, near the equator.

This argument as to the solar tide requires but little alteration to make it applicable to the lunar tide.

The positions of a set of "inverted" tides corresponding to the foregoing set of "direct" tides are shown in fig. 2.

Now since the rotation of the earth gives its surface an angular motion greater than that of the tide-producing body, its effect must be to carry

the protuberances forward towards positions which, according to the above interpretations, are in some cases more favorable for influence on the earth's rotation and in other cases less favorable, and if a wave is followed through its whole course, it sustains various relations, favorable and unfavorable, retardative and accelerative. The sum total of influences is thus seen to be a product of much complexity. It has been held that the retardative positions predominate in effectiveness. The case has usually been treated on the assumption of a continuous ocean belting the earth and permitting the tides to follow the tidal forces consecutively about the earth. It will be shown later that this is not the actual case, and that the tides are essentially limited to individual water-bodies. This further and greatly complicates the case. The problem is still further complicated by the past relations of the moon to the earth, and this claims attention before further considering the efficiency of the tides.

## THE GENESIS OF THE MOON.

- (1) The hypothesis of Laplace in its original form took no account of tidal action. Under it the rotation of the earth, when it had become condensed to a molten globe, was assumed to have had the velocity which at an earlier stage was necessary to separate the lunar ring, plus that which was added by subsequent contraction. How this high rate of rotation was reduced to the existing rate was not explained.
- (2) The supplementary hypothesis of Sir George Darwin replaces this defect of the Laplacian hypothesis by postulating a centrifugal separation of the moon-mass from the earth-mass after the parent-body had been condensed to a liquid or perhaps even incipient solid state, and a subsequent recession of the moon by tidal influence, accompanied by a reduction of the earth's rotation as its dynamic reciprocal. The postulated method of this tidal action has been stated above. The fundamental proposition that tidal friction will tend either to separate the two interacting bodies or to draw them together—according to the precise nature of their relations—is not questioned, as it seems to be solidly founded on the laws of energy, but it is necessary to consider the precise relations of the bodies to determine the character of the action under the preceding mode of interpretation, and we shall find occasion to question the mode itself. Darwin's method of starting with what was thought to be a fairly reliable astronomical indication of the present value of the earth-moon interaction and of working backward mathematically to the primitive state, or so far as the mathematical process would carry, is beyond praise. But as the present value of the earth-moon interaction is open to serious question and is not now replaceable by an unquestionable value, and as the postulates for the backward tracing are themselves in question, it is necessary to consider the hypothesis on more general lines. The value assignable to the tides in each of the earth's ages depends on the assumptions made regarding the physical states of the earth's interior. If the body of the earth be assumed to be molten, or viscous in such a degree that the body tides are important and are of the liquid or viscous type, the results will be very different from

those which will be reached on the assumption that the body tides are merely strains in an elastico-rigid earth. So, too, if the ocean has been growing in volume during the geologic ages, or has been changing in form in any notable degree, the results would need to be modified accordingly. Even when approached on the admirable lines of backward tracing by computation, the results are therefore subject to wide variation according as the postulates arising from one cosmogonic hypothesis are used or those of another.

If we were to follow carefully the first stages of the moon's evolution under Darwin's hypothesis, it would be seen how critically dependent that hypothesis is on an underlying theory of cosmogony. The moon is assumed to have been separated from the parent earth-moon mass by some form of centrifugal action. While the precise form may have been either one or another of two or more alternatives, the principle of action is the same up to a certain point and is best illustrated by supposing that the moon-mass separated as a unit, and that just after separation it was a spheroid close beside the earth-spheroid and revolving in the period of the latter's rotation. An objection to this supposition will be considered later.

Now at this critical stage the earth was subject to the tidal action of the sun, which, according to the fundamental theory of the hypothesis, should tend to retard the earth's rotation. The earth was also subject to contraction from loss of heat, which should tend to accelerate its rotation. If the former was the greater influence, the lunar tide, which would have begun to be generated as soon as a difference arose between the moon's revolution and the earth's rotation, must have fallen behind the moon's position and, according to the hypothesis, must have tended to draw it backward and bring it down to the earth. To permit the evolution to proceed at all it is necessary to suppose that the contraction from loss of heat was a greater influence on the earth's rotation than were the solar tides. Now, the earth's contraction from loss of heat at the present time is exceedingly small. If, therefore, the constitution of the earth has been much the same as it is now ever since its growth practically ceased, as assumed by one cosmogonic hypothesis, the supposition that the tidal evolution of the earth-moon system was started in the right direction for lunar recession by the superiority of the influence of contraction over that of the solar tides is either untenable or else the solar tidal influence was extremely small. The initiation of the tidal evolution postulated by this hypothesis is thus seen to be tied up with a very high rate of loss of heat in the initial earth-stages, and this is only assignable under certain cosmogonic assumptions which give to the earth a very hot surface. These are, however, not necessarily confined to the gaseous or meteoritic hypotheses. They may possibly be made under the planetesimal hypothesis, but in any case they are as speculative as the hypotheses themselves, and in the latter case somewhat less well grounded, because the alternative phases of the hypotheses seem to be the more probable.

It is worth while to note further in this connection that the evolution of the lunar tide, under the theory of Darwin, would be a very slow process,

and might be reversed before it escaped the critical conditions named above. The speed of the earth's rotation and the speed of the lunar tide in this early stage must not be confounded, for the speed of the tide is dependent on the difference between the angular rate of the earth's rotation and the angular rate of the moon's revolution. At the instant of separation the two rates were the same, and the tide, if the stationary protuberances caused by the moon can be called a tide at all, would be infinitely slow, and the period of the tide—the time required for the tide to make a circuit of the earth-infinitely great. At the first stage of difference in angular rate, if the earth's rotation was accelerated by contraction more than the solar tides retarded it, the movement of the tide would be infinitesimally slow in the present direction, and the tidal period sub-infinitely long. The movement of the tide over the face of the earth would be accelerated only as the contractional acceleration continued to be superior to the solar tidal retardation reinforced by the lunar retardation. If the rate of loss of heat, which must have declined rapidly as the supposed molten earth crusted over and the crust became thicker, fell below that at which its accelerating value on the rotation of the earth was superior to the retardational value of the solar and lunar tides, and the latter then became superior, the time of rotation of the earth might be forced back to coincidence with the revolution of the moon, and the lunar tides temporarily suspended and, a little later, reversed, and the moon brought back to the earth according to the fundamental postulate of the theory.1 To escape this contingency it is necessary to suppose that the contractional influence of the loss of heat continued to be superior to the retardational influence of the solar and lunar tides until the lunar tide, though developed with extreme slowness, had extended the moon's revolutionary period so much that when the retardational influence became superior to the contractional influence it was too late for it to reduce the rotation-period of the earth to the revolution-period of the moon at that end of the evolutional series. These considerations serve to indicate how delicately poised were the initial conditions assumed by the hypothesis and how completely they were dependent on the heat-emission of the earth at the critical stage, which in turn was dependent on the cosmogony that preceded it.

The argument that the balance of influence must have lain on the side of heat-loss or else the moon would not be where it is at present, would be pertinent if the earth-moon evolution were absolutely shut up to one or the other of the alternatives just considered, but it has no force against a hypothesis which entirely avoids these critical alternatives.

It is to be noted further that the tidal reactions in the initial stages of the hypothesis of Darwin must apparently have been those of the earth's body, for if the heat had been so far dissipated that the earth was crusted over and the oceans were permitted to mantle the earth, the loss of heat would possibly have been too small to start the evolution in the postulated direction. The atmosphere must then have been of that vast vaporous

<sup>&</sup>lt;sup>1</sup> The correctness of this is dependent on the soundness of the theory that the position of the tides determines their accelerative or retardative character, which will be considered later.

kind made so familiar to us by the geologic rhetoric of the last century. Until the outward reach of this atmosphere was escaped by the receding moon, the atmospheric friction must have kept the moon in consonant revolution with itself and tidal action could not have been inaugurated. This must have prolonged the critical stages and made the triumph of contraction over the solar tides all the more doubtful.

The separation of the moon from the earth after the common mass became a liquid spheroid is subject to another serious contingency, based upon the same principle of differential attraction as the tides themselves. Roche has shown that a satellite revolving within a given distance from its primary will be torn to fragments. The fragments must revolve at velocities strictly dependent on their distances from the center of the primary and hence must disperse themselves into a ring of the Saturnian type.1 fragments so produced would be subject to further reduction by collisions with one another, by changes of temperature, and by internal reactions, and would probably only reach an approximately stable condition as to size when they were well comminuted. For the earth-moon combination the Roche limit of disruption lies about 11,000 miles from the earth's The cogency of Roche's reasoning, supported by that of Clerk-Maxwell and others, and the example of the rings of Saturn, seems to leave no alternative but to suppose that a body of the mass of the moon could not pass from the earth outward by tidal reaction without being torn to fragments and converted into a ring, unless the fission of the earth-moon mass and the initiation of the lunar tide took place outside the Roche limit, which is difficult to believe under the Darwinian hypothesis, though consistent enough with the Laplacian. The laws of revolution seem to forbid the supposition that the fragments produced by tidal disruption could have been aggregated for any appreciable length of time on one side of the earth so as to act jointly in producing an effective tide. Even if some tide could be so produced there would still remain the question whether it would have carried the fragments outward by reaction sufficiently far for them to have escaped the dangers of reversal by the solar tides, as pointed out in a preceding paragraph. There seem to be no cogent theoretical grounds upon which it can be affirmed that the fragments of a disrupted body of this kind would evolve into any other condition than that of a ring of discrete particles during the time available for starting the recessional movement of the moon. They might perhaps move outside the Roche limit or be drawn down to the planet in a period sufficiently long, but probably not in the available period. The fact that the Saturnian rings are present at this stage in the history of the solar system suggests, if it does not definitely imply, that this form of organization is one of much persistence.

If we pass by these peculiar difficulties that embarrass the supposed separation of the moon from the earth, and if we set aside the special consequences assigned to a molten or viscous earth-body, the remaining

¹ On the stability of motion of Saturn's rings. < Scientific Papers of James Clerk-Maxwell, vol. 1, pp. 288-376.
² Darwin's "Tides," pp. 358-360.

problems respecting the influence of the tides on the earth's rotation are essentially the same, whatever the genesis of the moon, and so these further problems may well be deferred until it is seen where and how the various genetic theories come onto common ground and may be treated in a common manner.

(3) There is nothing in the planetesimal hypothesis that is, in itself, necessarily prohibitive of an origin of the moon by centrifugal separation from the earth-mass, for under it the planetary bodies may have had very high rates of rotation. So also the mass of the planetary nucleus may have been so large and the ingathering of the planetesimals may have been so rapid, by hypothesis, that a molten or even a gaseous condition could have arisen. In the case of the larger planets such a primitive state is quite within the limits of the probabilities. The case of the earth is debatable, but it will be of no service in this discussion to follow the gaseous or molten alternative, as it would be essentially identical with the preceding.

There are two other possible modes of origin of the moon, in neither of which was the moon-mass ever a part of the earth-mass. In both of these it is supposed that the nebular nuclei of the earth and the moon were separate knots of the parent spiral nebula. In the first case, they are supposed to have been companions in projection from the ancestral sun, and to have revolved about their common center of inertia from the outset. In the second case, the nuclei are supposed to have been at the outset independent knots having separate orbits about the sun but near one another. The two are supposed to have come into their present relations in the course of the segregation of the parent nebula. Rather grave dynamic difficulties attend this latter view, and it need not be pursued further here, as the rotatory problems under it are not essentially different from those of the first and much more probable alternative.

In this preferred alternative, the nuclei of the earth and moon, at the instant they left the ancestral sun, are supposed to have been a single mass which was given a forward rotation by the unequal resistances on its opposite sides to the expelling impulse, for which there are assignable reasons. Just after leaving the sun, the mass is supposed to have separated as an incident of the expulsion, but the two parts are supposed to have continued to revolve about their common center of inertia essentially as before, i.e., as a rigid body. After separation, however, each was subject to the rotational effects of the accession of planetesimals, and when their rotations came to differ from their revolution about the mutual center of inertia they were subject to tidal reaction. The extent to which such differences of rotation arose is an essential part of the problem under this hypothesis.

There were many possible alternatives, theoretically speaking, as to the relative sizes of these nuclei and the distances to which they separated under the initial impulse, but there were limitations to these. If the combined masses of the two nuclei were one-eighth of the combined mass of the present earth and moon, the moon could not have been more than 460,000 miles from the earth, but as this is farther than it is at present the

hypothesis is not hampered by this limitation. If the joint mass was larger, their initial distances may have been greater; if smaller, they must have been less. Within the limits thus imposed by the mechanics of the case, the nuclei may have been separated by any distance, abstractly considered, from the maximum permitted down to surface contact.

In fact, however, the degree of nearness consistent with the present state of things, was limited by the consequences of growth, for the increase of the masses of the nuclei by the ingathering of the planetesimals may have drawn the nuclei toward one another, or even together. This was conditioned by the moment of momentum which the accessions carried into the nuclei, which varied widely. Separation later by centrifugal action would be theoretically possible, under assignable conditions, but not at all inevitable, perhaps not at all probable. If the initial distance of the nuclei were sufficient, however, the nuclei might approach one another so long as growth was a ruling influence. Tidal action would run concurrently with this and would oppose approach, under most conditions, but during the more rapid stages of growth, the tidal effect may possibly have been less than the effect of increasing mass. But the tidal effect would increase as the bodies were drawn toward one another, while in the later stages of growth the increase of the mass would decline in rate. At a certain stage the two effects may be presumed to have balanced one another, after which recession would begin through the preponderance of the frictional effect of the tides. From that stage, the history would proceed along the lines determined by the mutual interaction of the matured bodies.1

It will be seen that the range of specific assignments under this phase of the planetesimal hypothesis has a wide amplitude, embracing the permissible assignments as to the original distances between the nuclei, as to the original masses of the nuclei, and hence as to the amount of their growth, as to their planes of revolution, their eccentricities of orbit, etc. Under this amplitude, it is possible to suppose that the two bodies at the climax of their approach reached precisely the relations which were indicated by Darwin in his backward tracing of their history. On the other hand, so far as the hypothesis itself is concerned, it is equally possible that the approach of the bodies was much less close, and hence that their recession under tidal influence was correspondingly less. It will be seen, therefore, that this hypothesis has very much greater adaptability than the hypothesis of centrifugal separation, and does not equally hamper us respecting subordinate hypotheses, such as a molten state, a viscous interior, or a particular amount or a particular distribution of the hydro-We are quite free to follow backward from the present observational data, when it shall be possible to do this on firm ground, with the utmost complacency as to the results, and to accept these as indicating the original relations, whether they imply a former state of coalescence, or of close approach, or of more distant approach. It is possible that the earth and moon were drawn together by their growth into just those relations which Darwin assigned to them when, in his backward tracings of their

<sup>&</sup>lt;sup>1</sup> The effects of contraction are here neglected.

history, his mathematics ceased to tell what lay beyond. At the same time. the hypothesis is hospitable to any smaller numerical values for the frictional effect of the tides which revised data may be found to imply.

We are now prepared to inquire with equanimity what is the degree of trustworthiness of the astronomic data relative to the recent timerelations of the earth and moon.

### THE EVIDENCES OF A PRESENT CHANGE OF ROTATION.

Near the middle of the last century Adams, from a study of certain data relative to the secular acceleration of the moon's mean motion, reached the conclusion that the earth was then losing time at the rate of 22 seconds per century. It is proper to add, however, that Adams laid but little stress on the actual numerical values which he used in computation, and that he was of the opinion that the amount of tidal retardation of the earth's rotation is quite uncertain.1 At a later date, Newcomb made a computation based on the data then available, with the result that the rate was reduced to 8 seconds per century.2 Darwin verified the computative part of Adams' results and added a neglected factor for the obliquity of the ecliptic and the diurnal tide which raised the estimate to 23.4 seconds per century. Newcomb's estimate similarly revised is 8.3 seconds.3

A reliable answer to the question whether the earth's rate of rotation is or is not now departing from constancy, and at what rate, depends not only upon extremely refined astronomical observations, but upon the interpretation of these observations by means of a perfect theory of the lunar motions. This latter has not yet been attained. In a case where the suspected variation from constancy is so slight, and where the logical structure to be built upon it in tracing it back through tens of millions of years involves so great a multiplication of any error it may contain, it is obvious that extreme accuracy and complete soundness are necessary to trustworthy results. In the judgment of cautious astronomers, these prerequisites are not yet attainable. It is not, therefore, too much to say that the deductions thus far made have not a sufficiently secure observational basis to give them authoritative value. This is not to say, by any means, that these results, based on the best data heretofore available, do not fully justify the elaborate mathematical investigations based upon them, for these have proved extremely illuminating and stimulative, and were almost necessary as precursors to the more critical work on both observational and theoretical lines which is necessary to give the firm foundation so eminently to be desired.

Tait's Natural Philosophy, II, p. 418.

Thomson and Tait's Natural Philosophy, II, p. 505.

<sup>&</sup>lt;sup>1</sup>Thomson and Tait's Natural Philosophy, II, p. 419; also pp. 415–520 and 503–505, edition of 1890, and the papers of Darwin previously referred to.

<sup>2</sup>Researches on the motion of the Moon, Washington, 1873. See also Thomson and

## DEDUCTIONS FROM THE TIDES THEMSELVES.

As astronomical observations thus leave it uncertain at what precise rate rotation is changing at the present time, it is necessary to fall back upon such other evidences as the tides themselves present, and after that upon the geological evidences. Each of the three fundamental divisions of the earth, the atmosphere, the hydrosphere, and the lithosphere, is affected differentially by the attraction of the moon and sun, and hence they are all, theoretically at least, affected by the tides. They furnish a suggestive combination for study in that the first is a highly fluent elastic body, susceptible of great and easy changes of form and volume; the second is extremely mobile, but sensibly incompressible; while the third is solid, at least externally, and probably rigid as a whole and possessed of effective elasticity of form. Because of the markedly different properties of these three components of the earth, it would seem that comparisons of their individual responses to the differential attractions of the moon and sun might throw special light on tidal phenomena.

### THE TIDAL PHENOMENA OF THE ATMOSPHERE.

Because the atmosphere is a highly symmetrical envelope, because its continuity is broken by no barriers, because it is extremely mobile, because it has great elasticity of volume, and because it presents greater differences of distance from the tide-producing bodies than the hydrosphere or the lithosphere, it would seem that it should give a tide of declared characteristics. We are, however, almost wholly without evidences of such a tide, notwithstanding the large mass of barometrical data at command. These data stretch over a long term of years and are refined enough to show several small periodic oscillations, but none of these, at least none of those commonly recognized, are timed with the moon. Atmospheric tides play no part in the science of modern meteorology. Laplace discussed the tides of the atmosphere briefly and theoretically and found that if the sun and moon were in the plane of the earth's equator and if the two bodies were in the same line and at their mean distances, the variation of the barometer would be 0.63 mm.1 Darwin, without entering upon their discussion, expresses the opinion that they are undoubtedly very minute.2 Other methods of estimating the atmospheric tides support Laplace in showing that the amount of the forced tides should be just within the limits of observation, from which it is inferred that they should become quite appreciable if they were much reinforced by the cooperation of free waves. The chief light which their scantiness seems capable of throwing on the general problem in hand is that which bears on the dependence of the actual tides upon the reinforcement of the forced waves by the commensurable action of the free waves that spring from them.

The best observational data relative to the rate of propagation of a free atmospheric wave arising from a forced oscillation are those furnished

<sup>&</sup>lt;sup>1</sup> Mécanique Céleste, Pt. I, Bk. IV, and Bk. XIII, vol. 5, p. 337. <sup>2</sup> Enc. Brit., "Tides," p. 353.

by the great explosion of Krakatoa on August 27, 1883, as set forth by Lieutenant-General Strachey in the monograph of the Royal Society on the "Eruption of Krakatoa and subsequent phenomena." He says:

The observed facts clearly establish that the successive repetitions of the disturbance at the numerous stations, after varying intervals of time, were caused by the passage over them of an atmospheric wave or oscillation, propagated over the surface of the globe from Krakatoa as a center, and thence expanding in a circular form, till it became a great circle at a distance of 90° from its origin, after which it advanced, gradually contracting again, to a node at the antipodes of Krakatoa; whence it was reflected or reproduced, traveling backwards again to Krakatoa, from which it once more returned in its original direction; and in this manner its repetition was observed not fewer than seven times at many of the stations, four passages having been those of the wave traveling from Krakatoa, and three those of the wave traveling from its antipodes, subsequently to which its traces were lost (p. 63).

The velocities of propagation of these waves were found to vary from 674 to 726 miles per hour—somewhat below the normal rate of sound at the surface of the earth, which is 757 miles per hour at 10° C. and 780 miles at 22° C. The average temperature of the air at its base is 15° C. to 17° C., from which the temperature declines with ascent, as does also the density.

The mean time occupied by the Krakatoan waves in making a first circuit of the earth, for the computation of which 27 stations were available, was 36 hours and 24 minutes, the angular rate being 9.89° per hour; the mean of the second circuit, for which 18 stations were available, was 36 hours and 30 minutes, the angular rate being 9.86° per hour; the mean of the last observed circuit, for which 10 stations were available, was 37 hours and 50 minutes, the angular rate being 9.77° per hour.

Now if the forced tidal wave be analyzed into instantaneous impulses

Now if the forced tidal wave be analyzed into instantaneous impulses and these be regarded as discontinuous, they may each be treated as though they gave rise to free waves similar to those derived from the volcanic impulses of Krakatoa. If we compare the intermediate rate determined for the free Krakatoan waves with the angular rate of the forced lunar tide, it will appear that the latter would outrun the former at the rate of about 4.6° per hour. The free wave would therefore soon begin to flatten the surface configuration of the forced tide by extending its amplitude, and in less than ten hours its influence would begin to be antagonistic to the forced tide. This antagonistic influence would reach its maximum about ten hours later, but would continue with declining force for nearly another ten hours, beyond which, because of the relatively high viscosity of the air, it may be regarded as negligible. It appears therefore that the periods of the free atmospheric waves are not such as to effectively reinforce the forced waves and hence they do not rise to appreciable value.

In addition to this there seems reason to suspect that the compressibility and the relatively high viscosity of the air may combine to cause a portion of the atmospheric tide to take the form of an elastic wave rather than of a fluidal movement; that is, the tidal force may produce alternate expansion and compression of the air such as would not be possible in water because of its incompressibility. Such expansional and compressional states of the atmosphere would be relieved by a prompt return to the unstrained condition as fast as the tidal forces were in any measure withdrawn

and this would reduce the amount of fluidal movement on which a masstide depends. It is not unlikely, therefore, that some part of the scantiness of the atmospheric tide is due to the elastic constitution of the atmosphere.

There is a semi-diurnal wave of atmospheric pressure which has its maximum about 10 o'clock a.m. and p.m. Lord Kelvin, interpreting this as an increase of mass corresponding to the increase of pressure, has computed that it would accelerate the rotation of the earth about 27 seconds per century.1 If however this oscillation is merely a transient increase of elastic pressure at the base of the atmosphere due to basal heat, the expansional effects of which are resisted for the time by the inertia of the air above, as seems not impossible, the wave would have no direct accelerative effects on the earth's rotation.

### THE TIDES OF THE LITHOSPHERE.

There is reason to suspect that the water-tides are in part derived from the pulsations of the lithosphere.2 It will therefore be best to discuss these first. Since no body is absolutely rigid, and since abundant evidence shows that the lithosphere is appreciably yielding, there can be no theoretical doubt that there are tides of the lithosphere of some kind and of some magnitude. The only vital questions therefore relate to their magnitudes and their specific forms.

The experimental efforts of Sir George and Horace Darwin,\* of Von Rebuer-Paschwitz,4 and of Ehlert,5 resulted in detecting only slight indications of body tides, and even these indications were of somewhat doubtful interpretation. It appears, however, that the effort of these investigators was directed toward the detection of the general deformations of the spheroid directly assignable to the tidal forces, and it is not clear that the observed results are to be interpreted as equally adverse to the existence of shorter pulsations assignable to the normal vibrations of the spheroid, induced by the tidal strains. The nature and likelihood of such shorter pulsations will be considered later.

So far as opinion as to the value of the lithospheric tides is entitled to weight we can not do better than to quote the conclusions of Sir George

¹ Natural Philosophy, Thomson and Tait, ed. 1890, p. 418.
¹ It should be understood that this is merely an individual view unsupported by the expressed opinion of any special student of the tides, so far as I know, and without recognition in the literature of the subject. It is based on the conviction that while the direct rise and fall of the surface of the lithosphere in response to attraction similarly affecting the water tends to reduce the amount of the water-tides, the tilting of the lithospheric bed in which the oceans lie first on one side and then on the other in the course of the progress of the lithospheric wave must develop an inertia tide very similar to the waves produced by the rocking of artificial basins. It is also my view that the various free pulsations that may arise from the forced deformations of the lithosphere may give impulses to the waters resting in basins on its surface and that water-waves may spring from these quite independently of the direct attraction of the tide-producing body, though of course indirectly dependent on it.

¹ Reports to the Brit. A. A. S. on Measurement of the Lunar Disturbance of Gravity, York meeting, 1880, pp. 93-126, and Southampton meeting, 1882, pp. 95-119; also "Tides," G. H. Darwin, 1893, pp. 108-148.
¹ Das Horizontalpendel, Nova Acta Leop. Carol. Akad., 1892, vol. 60, No. 1, p. 213; also Brit. Assoc. Repts., 1893; also Ueber Horizontalpendel-Beobachtungen in Wilhelmshaben, Potsdam, und Puerto Orotava auf Tenerifa, Astron. Nachrichten, vol. 103, pp. 194-215.
¹ Horizontalpendel-Beobachtungen, Beitrage zur Geophysic, vol. 3, Pt. 1, 1896.

Darwin relative to their present magnitude, remarking by way of precaution that the quotations given, separated as they are from their context and the qualifications it carries, are liable to convey misconception of the author's views on points other than that for which alone they are quoted here, viz. the magnitude of the tides of the lithosphere. He says:

The chief result of this paper [on Bodily tides of viscous and semi-elastic spheroids, and on the Ocean tides upon a yielding nucleus] may be summed up by saying that it is strongly confirmatory of the view that the earth has a very effective rigidity. But its chief value is that it forms a necessary first chapter to the investigation of the precession of imperfectly elastic spheroids, which will be considered in a future paper. I shall then, as I believe, be able to show, by an entirely different argument, that the bodily tides in the earth are probably exceedingly small at the present time.

And again, at the end of the later paper referred to:

The conclusion to be drawn from all these calculations is that at the present time the bodily tides in the earth, except perhaps the fortnightly tide, must be exceedingly small in amount; that it is utterly uncertain how much of the observed 4" of acceleration of the moon's motion must be referred to the moon itself, and how much to the tidal friction, and accordingly that it is equally uncertain at what rate the day is at present being lengthened.

It has already been made clear that Darwin's inquiry involved the assumption that in an earlier state, when the earth was more largely molten or viscous, the body tides were much greater and more effective than now. But if we substitute the view that the rigidity of the lithosphere has been nearly what it is at present through the whole history of the earth, as is permitted by the planetesimal hypothesis, the conclusions quoted will apply to the whole period, with such modifications as may be required for differences of distance between the earth and moon.

The substitution of an elastico-rigid earth for a viscous one affects the rotational influences of the tides qualitatively also. If tidal deformation causes a movement of the molecules of the lithosphere over one another in fluidal fashion, friction is the result, and the tide, under present conditions, must have a retardational influence. If, on the other hand, the molecules are merely strained elastically in their relations to one another, but do not shift these relations as they do in fluidal motion, the strain and the resilience from it act almost coincidently with the straining force, the original form and relations are almost perfectly restored on relaxation, the friction is slight, and the rotational effect will be essentially negligible.

Now, when it is considered that a tidal protuberance, at the very most, can warp a line of molecules only in some such measure as  $\frac{1}{5.000.000}$  to  $\frac{1}{15.000.000}$ , it seems clear that the deformation lies far within the strain-limits of crystalline rock, and probably within the strain limits of all rigid substances in the lithosphere. The only known substances within the outer half of the lithosphere that probably move as fluids under tidal stress, are the relatively trivial threads, tongues, or pools of lava within it, and the isolated molecules or groups of molecules here and there in the free form in the rigid rock. If we postulate an earth of such a degree of elastic rigidity

<sup>&</sup>lt;sup>1</sup> Phil. Trans. Roy. Soc. Lond., 1879, p. 31.
<sup>2</sup> On the precession of a viscous spheroid, etc. < Phil. Trans. Roy. Soc. Lond., Pt. II, 1879 (1880), pp. 483–484.

as seems to be required by the concurrent evidences of astronomical, geophysical, and seismic phenomena, it seems quite inconsistent to suppose that a brief deformation of the tidal sort can be other than a minute, highly distributive strain, which involves no flowage motion of the molecules upon one another, with the exceptions noted, and hence no friction of the fluidal type. There is a large body of geological evidence which seems to indicate that the lithosphere is able to accumulate stresses for long periods, which are then relieved by permanent deformations. It is difficult to understand how an earth could be possessed of this ability, if it yielded fluidally to such transient and moderate stresses as those of the tides of the outer part of the lithosphere. We therefore assume with confidence that, whatever the amount of the lithospheric tide, it is only an elastic strain which relieves itself almost instantly on the removal of the force which caused it and involves little friction.

It does not appear probable, therefore, that the body tides of the earth, under this view of the earth's constitution, are an efficient agency in reducing its rotation.

This conclusion, however, even if fully accepted, does not appear to cover the entire possibilities of the case; for, even if the primary tidal deformation of the lithosphere has little or no rotational effect, it may possibly give rise to pulsations in the spheroid itself which will be communicated to the water upon its surface and give rise to water-tides. If the periods of these pulsations are commensurate with those of the water-bodies arising from the direct attraction of the moon and sun, they may add something to these by sympathetic action, even though their independent value might be inconsiderable. This leads to an inquiry as to the natural oscillations of the spheriod and their relations to the oscillations of the lunar and solar tides.

# THE PULSATIONS OF THE LITHOSPHERE.

It appears to be possible to reach an approximate determination of the fundamental susceptibilities of the lithosphere to oscillations of different classes by combining the good offices of theoretical computations and observational inductions. The types of oscillation which need to be considered here embrace those which traverse the interior as well as the surficial parts of the earth as distinct waves of propagation, and those oscillations of shape which affect the form of the earth as a whole. The latter are treated as harmonic pulsations and may spring either from the transmitted oscillations or from differential stresses arising from variations of attraction. The data relative to transmitted oscillations have been furnished chiefly by seismologists; the treatment of harmonic pulsations and fundamental susceptibility to such oscillation has thus far been chiefly mathematical.

Lamb, following earlier work by Kelvin, has shown that several different species of harmonic oscillations may arise from both the longitudinal and transverse waves transmitted through the earth. For a steel body of the size of the earth, he found the period of the slowest fundamental mode of

<sup>&</sup>lt;sup>1</sup> On the vibrations of an elastic sphere, by Horace Lamb. < Proc. Lond. Math. Soc., vol. 13, 1882, pp. 189-212.

oscillation which assumed the form of a harmonic spheroid of the second order to be 78 minutes. A series of other oscillations of lesser lengths would be developed. He found that the compressibility of the matter is not a vital factor, for if t be the time required by a wave of distortion to traverse the earth's diameter, and if P be the period of oscillation of shape, then P=t 0.848 if the material is incompressible, and P=t 0.840 if the material preserves uniconstancy. Bromwich, bringing into the computation the effect of gravity, found that the gravest free period of a spheroid of the size, mass, and gravity of the earth, with a rigidity about that of steel, is 55 minutes. The corresponding period, if the effect of gravity be neglected, is 66 minutes. If the rigidity be about that of glass, the period is 78.5 minutes if the effect of gravity be included, and 120 minutes if gravity be neglected.

Nagaoka 2 has made a study of the pulsations connected with the Krakatoan eruptions of August 26 and 27, 1883, as recorded by the gasometer at Batavia, 94 miles from Krakatoa, on the supposition that these pulsations were derived directly from the volcanic explosions and thus registered their relative times. He reached the conclusion that the series of eruptions were rhythmical with a unit-period of 67 minutes and a tendency toward the grouping of these shorter periods into larger ones of about 200 minutes. The former he interprets as an expression of the fundamental period of oscillation of the earth as a spheroid. Referring to the results of Bromwich, he cites the coincidence of the Krakatoan periods so deduced with the computed periods when the assumption is made that the rigidity of the earth lies between that of steel and that of glass. Nagaoka also cites the apparent relationship of this period to seismic phenomena, and the apparent connection of certain of these phenomena with the Chandlerian nutation of the pole.

The correspondences may be carried appreciably further. While exact determinations of the velocities of seismic tremors recorded at a distance from an earthquake are not yet available, the time required by the foremost waves to traverse the earth's diameter may be taken provisionally at 22.5 minutes. These vibrations are generally interpreted by European and American seismologists as compressional waves and as passing through the earth along chords, or along curves of adaptation departing slightly from chords. The second set of tremors, generally interpreted as distortional, require about 50 per cent longer for chords up to 140°, and perhaps up to 180°, which would make their diametrical period about 33.75 minutes. For the chords between 140° and 160°, and perhaps up to 180°, Oldham inferred a longer period from the available observations, which are, however, thus far not sufficiently numerous for positive conclusions. These problematical vibrations may be directly transmitted or may be reflections. The period deduced for them is approximately double that of the compressional waves. The foremost large seismic waves, which have approximately a uniform velocity and which are interpreted as following

On the influence of gravity on elastic waves, and in particular on the vibrations of an elastic globe, by T. J. A. Bromwich. < Proc. Lond. Math. Soc., XXX, 1899.</li>
 Nature, May 25, 1907, pp. 89-91.

the surface of the earth, pass from the point of origin around to the antipodal point in about 112 to 115 minutes. The largest and strongest group of these large waves takes about 135 minutes. Comparing these with one another, it appears that the period of the maximum group of the large waves is six times that of the compressional waves, the former, however, traversing a semicircumference and the latter a diameter. The period of the second set of short vibrations for most chords is one-half more than that of the first set, while that of the problematic set is approximately twice that of the first set. Three times the period of the compressional waves, twice that of the best recorded distortional waves, one and a half times that of the problematic waves, and half that of the maximum long waves are each approximately 67.5 minutes, or essentially the same as Nagaoka's unit-period for the Krakatoan pulsations. The gasometer record of the Krakatoan eruptions is rather coarse and can not be read with exactness, but, taking Nagaoka's readings, the discrepancies between the recorded times of the twelve eruptions of August 27 and the periodic times on the 67.5 minute basis are as follows in minutes: 0 (starting-point, first eruption on August 27); -29 (=-33.5, the half period, +4.5); +14; -1.5; +2; +16; -3.5 (strong); + 3 (strong); +23.5 (=22.5, one-third period, +1); +33.5 (half period); -1.5 (the great eruption); -9 (the final eruption, strong). In the interpretation it is assumed that the eruption of August 26 at 5<sup>h</sup> 20<sup>m</sup> p.m. started a series of oscillations in the lithosphere which, at the end of the sixth period of 67.5 minutes, with a lag of 4 minutes, had developed sympathetic relations with the volcanic forces and stimulated the first of the twelve eruptions that followed. These have the degree of correspondence to the assumed period just shown. Each eruption falling at or near the critical stage of the pulsation previously developed may be supposed to have strengthened the succeeding oscillations until the series reached a first double maximum at the seventh and eighth eruptions, and a second and greatest maximum at the eleventh and twelfth. If this interpretation be justified, it may mean that the vibrations which arose from the earthquake developed into the form and periodicity of the fundamental vibrations of the earth-spheroid. The inadequacy of the data, quantitatively and qualitatively, to establish this positively is obvious, and it may not be safe to rest much upon it; but the following are curiously related to it.

The moon's synodical period, 1,490.5 minutes, is 22 times 67.75. The solar period, 1,440 minutes, is about 21.25 times 67.75. If 67.75 minutes be taken as the normal period of spheroidal oscillation, 22 of these constitute a lunar day, 314 approximately the average fortnightly excursion of the moon north and south of the equator, and 628 the lunar month. If a represent the northerly fortnightly excursion, and a' the southerly, each of these equaling 314 earth-pulsation periods, they will obviously have close commensurate relations at the periods represented by aa', a(a+a'), and  $(a+a')^2$ , whose numerical values are 218, 436, and 870 days, respectively. Now, 436 days is the recent estimate of Kimura 1 for the

<sup>&</sup>lt;sup>1</sup> Physico-Math. Soc. Tokyo, Pt. II, 24, pp. 357-364, 1905; Sci. Obs., July 25, 1906. Pop. Astr., Oct. 1906, p. 469.

larger circular element of the Chandlerian nutation of the pole, and this period of Kimura is perhaps to be regarded as a closer approximation than the earlier estimates of 427 to 430 days. As the sums of the tides formed when the moon is on the equator, is north of the equator, and is south of the equator, respectively, are different from one another, partly because of the differences in the moon's position and partly because of differences in the configurations of the lands and seas on the two sides of the equator, there seems to be a fair presumption that there would be a periodic difference in the tidal influences on the rotation of the earth about its axis corresponding to the fortnightly excursions, which would express itself in a nutation. Now if this period of forced nutation happens to be commensurate with the free period of the earth as a rotating body, the effect would be cumulative. Euler long ago computed that the period of free nutation of the axis of the earth, if it were an absolutely rigid body, would be 305 days. Newcomb, on the assumption that the earth has the rigidity of steel, found that the period would be increased to 447 days. This seems to imply that the earth is somewhat more rigid than steel and has a free nutation period somewhere about 427 to 436 days. As the fortnightly group of tides have a cumulative period commensurate with the latter, the nutation of 436 days may perhaps be due to the agency of this tidal group.

In addition to this larger circular nutation, whose radius is about 15 feet, there is a smaller elliptical nutation, of about 4 feet by 14 feet, with an annual period. This is assignable to the annual migration of the sun north and south of the equator, which gives rise to a variety of dynamic effects in the form of changes in the circulation of the atmosphere and of the ocean, in the accumulation and melting of snow and of ice, etc. This is in line with the common explanation of this minor nutation.

It is an established principle that when the normal period of oscillation of a body is less than the period of the periodic force acting on it, the oscillations of the body will agree in phase with those of the force. On this principle the oscillations of the lithosphere should agree in phase with the period of the tidal forces. There should therefore be direct cooperation between the waves of the lithosphere and the forced water-waves. On account of this close coincidence there is an obvious difficulty in distinguishing the contributions of the lithosphere to the water-tides from those tides which spring directly from the attraction of the tide-producing bodies. The two should merge into a common tide, but, if the view here entertained relative to the development of water-tides through oscillations of the lithosphere be valid, the actual tides are to be regarded as composite.

If the tides of the lithosphere were of the fluidal type and acted in strict coincidence with the water-tides, they would reduce the latter to the extent of their own magnitude, as urged by Kelvin and Darwin; but in so far as the pulsations of the lithosphere have the effect of a series of tiltings of the basins on the lithospheric surface, they must impart oscillatory movements to the water held in the basins. It is safe, on observational grounds, to

<sup>&</sup>lt;sup>1</sup> Thomson and Tait, Natural Philosophy, Pt. II, p. 439.

affirm that all the oceans behave, in the main, as if they were isolated bodies held in basins on the surface of the lithosphere. There are no effective tidal belts stretching around the earth parallel to the equator and furnishing an opportunity for the development of a continuous tide of the canal type. The Southern Ocean, once regarded as such, does not prove to act in this way, nor do the Pacific and Indian Oceans act as a common body, as represented on the old tidal charts.1 For the purposes of this discussion it may be assumed with practical safety that the seas occupy a chain of irregular basins linked to one another in various unsystematic manners, and that each of these bodies is subject, in its own way, to such oscillations as the rocking of its basin may impart to it. If the tides of the lithosphere are as small as present evidence seems to indicate, this may not be important in its own first effects, but as a periodic action it may become, by commensurate accumulation, a not unimportant factor. Some of the peculiar features of the tides seem to be much more intelligible on the supposition that they arise from the oscillations of the lithosphere than from the direct action of the lunar and solar attractions. The rocking action of the basins would generate tides as freely on the eastern as on the western sides of the oceans, whereas the attraction of the moon and sun should be accumulative toward the western side. The tides are, however, rather higher on the eastern than on the western sides of the oceans. We shall have occasion to return to this significant feature.

When a strain, or a deformation, or a movement of any kind is being impressed with increasing or declining intensity upon an elastic body which is already in a state of constant pulsation, as is the lithosphere, the superimposed action becomes itself pulsatory, however continuous and uniform the increment or decrement of the superimposed action may be in itself, for the existing pulsation of the body alternately opposes and coincides with the superimposed action and gives it a corresponding pulsation. The water-tides assigned to the rocking of the containing basins may therefore be treated as composite pulsations, each advancing and each declining phase consisting of an undetermined number of pulsations, each of which gives rise to its own partial free wave. These, as do all waves of whatever source, react on the lithosphere. Each such reacting pulsation, so far as it takes the form of a compressional wave, passes through the lithosphere to the antipodes in about 22.5 minutes. It there constitutes an impulse acting at an angular distance of about 5.6° in the rear of the corresponding part of the antipodal wave, tending, in its minute degree, to strengthen it, but with a slight increase of amplitude. The return of this wave requires an equal period which brings it into action at about 11.2° in the rear of the crest of the wave from which it sprang. This wave will therefore act several times in an approximately commensurate way before any appreciable incommensurate effects will be developed, and by that time its force will largely be spent. In so far as the reaction of the original wave develops an undulatory wave on the surface of the lithosphere, this wave will reach the antipodes in about 2.25 hours and will act in a

<sup>&</sup>lt;sup>1</sup> See Tidal charts of the U. S. Coast and Geodetic Survey, Rept. Sept. 1900, App. 7, Outlines of Tidal Theory, Pt. IV A, Rollin A. Harris. Also Pt. IV B, 1904.

similar way on the antipodal wave, tending to increase its amplitude and to reduce its surface gradient. On its return it will fall so far behind the original wave as to have appreciable incommensurate effects. The waves of intermediate period will have corresponding intermediate effects. In so far, therefore, as water-waves react upon the lithosphere and develop waves in it, these, while cooperating with the original waves commensurably for a time, will tend to distribute the oscillatory action into broader amplitudes. This may be looked upon as a tendency to develop a distributive series of small pulsations in lieu of the original more concentrated one. It is observed that small pulsations attend the incoming and outgoing of the tides, but they have not, so far as I know, been made the subject of sufficient study to determine whether they are systematic or irregular, and whether their periods are at all in accord with the natural periods of the lithosphere or not.

It is assumed in the foregoing that tidal pulsations will move through and over the lithosphere at the same rate as seismic pulsations, which probably does not involve any essential error, though pulsations vary somewhat in their speed, even when of analogous classes. But only the general order of velocity is of special moment here.

According to the mathematical investigations of Lamb, there should be a double series of modes of oscillation in the spheroid derivable from the initial impulse, of which one set should spring from the compressional waves and another set from the distortional waves, and these should differ in period. Only the gravest periods have been cited above. Without attempting to determine what these shorter periods are in the case of the lithosphere, it is probably safe to say that such as are commensurate with the tides of any body of water would cooperate to build these tides up and such as are incommensurate would have the opposite influence. Now if the tides of each body of water are essentially individual and are radically influenced by the breadth, depth, and configuration of the water-body, it is not improbable that different species of both series of natural pulsations may cooperate with the tides of different oceans and assist in their perpetuation and development.

If the distribution of the strains developed by increasing or diminishing attraction takes place at a velocity similar to seismic vibrations, even the larger tidal movements of the lithosphere will act almost simultaneously with the tide-generating forces, for no strains of the same phase will extend more than 4,000 miles from the center of development of that phase. The extreme movement from the center to the circumference of the strained area would occupy, at the observed rate of compressional waves, less than 12 minutes. In so far, therefore, as retardation of the earth's rotation is dependent on lag of the tide, it will be inconsequential for this class.

Relative to the tides of an elastic earth, Darwin says:

The other hypothesis considered is that the earth is very nearly perfectly elastic. In this case the semi-diurnal and diurnal tides do not lag perceptibly, and the whole of the reaction is thrown on the fortnightly tide, and moreover there is no perceptible tidal frictional couple about the earth's axis of rotation. From this follows the remarkable conclusion that the moon may be undergoing a true secular acceleration of motion of

something less than 3.5" per century, whilst the length of the day may remain almost unaffected.

The results of these two hypotheses (a viscous spheroid and a nearly perfectly elastic spheroid) show what fundamentally different interpretations may be put to the phenomenon of the secular acceleration of the moon.

Under these circumstances, I can not think that any estimate having any pretension to accuracy can be made as to the present rate of tidal friction.

### THE TIDES OF THE HYDROSPHERE.

If the preceding views are tenable, practically the whole tidal effect on rotation at present is concentrated in the water-tides. A part of these are assigned to the immediate action of lunar and solar attraction and a part to the mediate action of the lithosphere. While the lithosphere is thus supposed to contribute to the formation of the water-tides, this supplementary action is supposed to be qualified by its distributive action as previously explained. The water-tides are thus interpreted as more complex in origin than they have usually been thought to be. This must doubtless be regarded as an unwelcome infliction, for even under the simpler conception of their origin from direct attraction only, they are, in many of their phases, beyond complete mathematical treatment. These added complexities put them still further beyond the reach of such treatment. But this added complexity may, after all, only help to force us on toward the adoption of naturalistic methods. It has been becoming increasingly clear for some time that, to secure reliable results, the tides must be studied on a direct observational basis. The more hopeless the purely theoretical method becomes, the more assiduously is the observational method likely to be pursued. If theoretical methods are given precedence, they should be such as are based on the fundamental laws of energy, which hold good irrespective of special forms of action, however multitudinous and irresolvable.

As already remarked, the tidal water-bodies have no systematic, much less have they any symmetric, distribution. Innumerable idealizations as to the forms and relations of the oceans have been framed, but beyond a few of a very general sort, they are notable principally for their undue emphasis of amenable concurrences and their neglect of refractory non-concurrences. The north-south extensions of both the eastern and western continents are particularly unfavorable for the development of a continuous forward movement of the tides. The southern ocean furnishes the only continuous east-west belt of ocean encircling the earth's axis of rotation, but, according to the cotidal charts of the U. S. Coast and Geodetic Survey, this is not affected by a continuous westerly tide. The Pacific tides move easterly from New Zealand and, by interpretation of the scant data available, easterly all the way to the straits between South America and Antarctica, through which they move eastward and then northward along the Patagonian coast. The tides of the northeastern part of the Indian Ocean move easterly into the straits between Australia and Asia, while the Pacific tides enter on the opposite side and the two sets

<sup>&</sup>lt;sup>1</sup> On the precession of a viscous spheroid, etc. < Phil. Trans. Roy. Soc. Lond., Pt. II, 1879 (1880), p. 529.

meet one another within the inter-island water-bodies. There seems to be no definite perpetuation of the Pacific tides into the Indian Ocean, these bodies, though connected both north and south of Australia, acting in essential independence. While the long-prevalent view that the tides of the Atlantic and Arctic Oceans are derivatives from the Southern Ocean still has the apparent support of observational data, there are many facts that seem to indicate that this is only a part of the truth. A derivative wave should gradually die down as it progresses; but, notwithstanding the distance of the North Atlantic from the Southern Ocean, the tides are higher there than those of the South Atlantic. A derivative wave should be intensified in passing a constriction and should be lowered in an expanded water-body beyond; but, notwithstanding the reduction of the Atlantic breadth between Brazil and Sierra Leone, the tides are particularly high in the lee of the great nose of Africa north of this constriction. The northeasterly-trending coast of New England and the Provinces stands directly athwart an unobstructed stretch of sea reaching back to the Southern Ocean along the line of assumed propagation, and yet the average tide on this coast is notably less than that on the European coast of the same latitudes, though this lies behind the African projection. Comparing the tides on the Atlantic islands—whose isolation should render them measurably free from local influences, save those of their own basal slopes and their harbors—it is notable that the tides on the islands of the South Atlantic average less than half as much as those of the islands of the North Atlantic. The tides on the islands in the far North Atlantic, and even some of those in the borders of the Arctic Ocean, are singularly high, such as those of the Faröes, Shetlands, Orkneys, Hebrides, Iceland, Greenland, Jan Mayen, and some Arctic Islands of North America. On the purely derivative theory, these tides must be supposed to have been traveling 24 hours or more since they left the place of their origin, and those in the high north have been subject to the damping effects of polar ice.

There are not a few anomalies that are very puzzling on the supposition of a westward drag of the waters by the moon and sun. The northeast coast of South America trends northwesterly and the Central American states continue the trend in fair alignment. Over against this, the North American coast has a southwesterly trend, meeting the projection of the northwesterly trend of South America on the coast of Guatemala, thus forming a wide eastward-facing angle. From this point to Cape Race, the angular distance is 40° and from it to Cape St. Roque, 50°, while the open eastward-facing mouth between Cape Race and Cape St. Roque is about 50°. On the hypothesis of a westward-moving tide, cumulative toward the west, we should expect high tides in the Antilles, the Caribbean Sea, and the Gulf of Mexico. If it is thought that the last two bodies are protected from this high tide by the Antilles, the tides on the eastern side of the Antilles should be markedly high. The record does not show this. The tides on the African and European coasts opposite are notably higher than those which might be supposed to be unusually concentrated within this angle. As bearing on any supposed protection of the Gulf of Mexico and the Caribbean Sea by the Antilles, a comparison may be made with

Hudson Bay, which is far more land-locked and is in a much higher latitude and much farther from the assigned source of derivation. Singularly enough, the tides in Hudson Bay are several times as high as those of the Mexican Gulf and the Caribbean Sea.

If it be objected that the North Atlantic is too narrow and too peculiar in its relations to give these singular features much weight, a similar line of inspection may be applied to the Pacific, whose breadth and equatorial position make it preëminently favorable for a westward accumulation of the tide. From the mass of data now made available by Harris's compilations and harmonic reductions, it appears that the tides on the eastern side of the Pacific as recorded on the American coasts are notably stronger than the average tides on the Asiatic coasts. A comparison of the tidal heights on the Pacific islands, though the data are inadequate, also fails to show a concentration on the western side.

On the old cotidal charts, and more definitely on the new ones of Harris (fig. 3), it appears that the dominant tide of the Pacific originates in a singular loop near the Galapagos Islands, off the coast of South America, from which, on one side, a wave moves easterly and southeasterly to the South American coast in strong force, then down it to the extremity of the continent, where, according to Harris, it rounds Cape Horn and moves up the eastern coast of Patagonia to about the mouth of the Rio de la Plata. On the other side of the Galapagos loop, a wave moves northwesterly along the North American coast, and then westerly toward the Asiatic coast. In the heart of the Pacific, Harris locates three amphidromic centers of practically no tide (fig. 3). While these are not directly based on observations, they are believed by this industrious and original student of the tides to be in accord with the data derivable from the observed tides of the central Pacific Islands. This singular dispersion of the Pacific tides from the vicinity of the Galapagos Islands near the eastern border of the great ocean, as shown on the old charts, suggested to me, perhaps a decade ago, that the water-tides might be largely derived from the lithosphere rather than directly from the attraction of the moon and sun on the water itself. The rocking of the basins, first by a lift on the east side and later by a lift on the west, under the progressive influence of the tideproducing body, seemed to me more compatible with this behavior of the tides than direct attraction on the water itself, which I supposed should be less effective on the east side than on the west. The greater strength of the tides on the east side of the Atlantic also strengthens the impression that, whether this suggestion of derivation from the pulsations of the lithosphere be of any value or not, the actual evolution of the tides involves much more than the simple upward pull and westward drag of the waters by the moon and sun.

The recent theory advanced by Harris, that the tides are largely due to the cumulative agency of stationary oscillations in such segments of the oceans as may act commensurately with the tidal forces, goes far to relieve the foregoing and similar features of the tides of their seeming

<sup>&</sup>lt;sup>1</sup> "Outlines of tidal theory," Rollin A. Harris, Rep. U. S. Coast and Geodetic Surv. 1900, app. 7, pp. 535-699.

incompatibility with the theory of direct attractional action on the water itself; indeed, the concrete features of Harris's theory seem to have been developed largely by a study of these remarkable features, and to be an attempt to give them a dynamical expression in terms of the direct-action hypothesis. Whatever shall be the final judgment regarding particular aspects of this theory, whose author claims for it only a partial explanation of the tides, it seems eminently probable that commensurate oscillation is a vital factor in building up the waves of the actual tides. The attempt to work out a concrete theory of the tides from their specific phenomena is greatly to be commended, for by concrete application alone are the proximate sources of the tides likely to be determined. This may be said without derogation of the value of the more general theories.

Concerning the insufficiency of simple attraction without sympathetic intensification to explain the actual tides, Harris says:

In approaching the question of the actual causes of the tides, upon which so much labor has been expended and concerning which so much has been written, one may well surmise that the subject does not admit of accurate or complete treatment. It is therefore natural to consider, in the first place, only those sources which would seem to account for the dominant tides in any given region under consideration, and to postpone, perhaps indefinitely, the consideration of those sources whose importance in the production of the tides must be relatively small. Considering the actual distribution of land and water a few computations upon hypothetical cases will suffice to convince one that as a rule the ocean tides, as we know them, are so great that they can be produced only by successive actions of the tidal forces upon oscillating systems, each having as free a period, approximately the period of the forces, and each perfect enough to preserve the general character of its motion during several such periods were the forces to cease their action.

In another place he says:

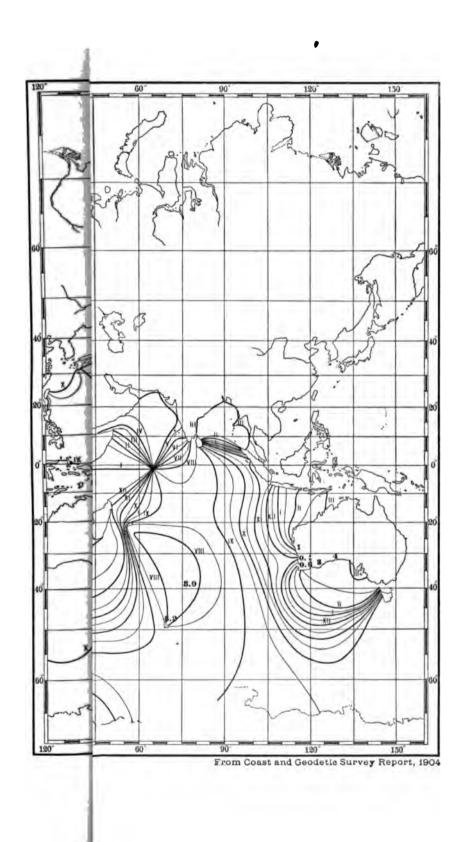
Unless the free period of a body of water, or of some portion of this body, approximately agrees with the period of the tidal forces, the tide in the body proper must be small, and generally smaller than the theoretical equilibrium tide for the body in question. But in many parts of the oceans, the tide is several times greater than that which could be raised by the forces, even if we could suppose sufficient depths and sufficiently complete boundaries for enabling equilibrium tides to occur. Hence regions the dimensions of which approach critical values must exist in the oceans and account for the principal tides.

That stationary oscillations of unexpectedly large amplitude exist in the oceans there is abundant evidence. In fact, a glance at the charts will show regions of large ranges over each of which the time of the tide varies but little. As a nodal line is approached the range diminishes, and the time of the tide changes rapidly in a comparatively short distance. Moreover the dimensions of the oceans are such that areas having nearly critical lengths can be readily discovered; these respond well to the forces, and their tides must be the ruling semi-diurnal tides of the ocean.<sup>2</sup>

Harris has attempted to detect those portions of the oceans whose lengths, depths, and relations make them susceptible to the development of free oscillations whose periods are sufficiently near to the periods of the tidal forces, or to some simple fraction of them, to permit coöperation in building up effective stationary systems of oscillations. Of the major order, he finds a northern and a southern system in the Indian Ocean, a South Atlantic system, a North Atlantic system, and two systems in the Pacific, as well as a large number of systems of the minor order. Diagrams and details of the main systems are given in the original paper.

<sup>&</sup>lt;sup>1</sup> Loc. cit., p. 624.

<sup>&</sup>lt;sup>2</sup> Nature, Feb. 22, 1906, p. 388.



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Harris does not claim that the demonstration of these is complete or final, and he recognizes that much additional data will be required for a full verification of the postulated systems and for completing the full category of systems, but he believes that those announced correspond fairly well with existing knowledge. Question has been raised as to whether the phases of oscillation which he assigns to his systems are such as would naturally arise from the forced waves. Question has also been raised as to the adaptability of the oceanic segments to oscillate as postulated. Harris contributes a new map of cotidal lines for the world (fig. 3) in which interpretation is conveniently combined with the observed data which are also given separately in tables and in sectional charts. By comparison of this cotidal map with previous charts, it will be seen that Harris's interpretation departs rather markedly from that implied by the previous cotidal charts.

A significant feature of Harris's cotidal map is its amphidromic nodes, centers of little or no tide about which the tidal wave swings in the course of the twelve-lunar-hour period. Three of these amphidromic points are located in the Pacific, one in the North Atlantic, and one in the Indian Ocean (fig. 3). These points are associated with nodal lines that separate the oscillating sections of the systems to which they are assigned. That there should be such nodes of little or no tide in the heart of the great oceans, where under the familiar mode of interpretation the tidal waves should have their freest sweep and greatest strength, well expresses the extent of Harris's interpretational departure.

It appears then that, under the broad mantle of the postulate that the tides are due to the attractions of the sun and moon, there are three special or proximate views as to the immediate origin of the actual tides: (1) the direct attraction of the tide-producing bodies on the water; (2) the effect of stationary oscillations promoted by such direct attraction; and (3) the to-and-fro tilting of the rock basins in which the water-bodies rest by the tides of the lithosphere. The older view has always recognized the supplementary effect of the natural oscillations of the water-bodies, but it has never given them a prominent place nor quite that distinctive form which has been assigned them by Harris. Since the cooperation of oscillations is independent of their source, any waves that may come from the lithosphere are as available for building up systems of stationary oscillations as are those springing from direct attraction, since they are likely to be timed quite as well. Harris's theory, or any theory of its kind, may therefore find as good a working basis in tides derived from the lithosphere, so far as these go, as in those formed by direct attraction.

The vital question here is the bearing of the deductions from these three points of view—assuming that each of them represents some truth—on the rotational problem. Let us first consider this on the familiar assumption that retardation is dependent on the position of the waves, assuming that to produce retardation the wave on the moonward side must be in front of that body pulling it forward and being itself in turn pulled backward

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<sup>&</sup>lt;sup>1</sup> Nature, Sept. 4, 1902, p. 444; Apr. 23, 1903, p. 583; Jan. 11, 1906, p. 248; Feb. 22 1906, p. 388.

over the earth's surface (figures 1 and 2). Afterwards let us consider the phenomena from a more radical point of view founded on the laws of energy and the configuration of the interacting bodies.

From what has already been said, it is clear that no continuous tides are being dragged around the earth acting as a frictional band. No single tide moves westerly so much as one-half of the earth's circumference, and most of the tides have a much less movement in that direction. On the other hand, many tides move easterly and still others move northerly and southerly. The position of these relative to the moon is various, and the attraction of the moon upon them may be accelerative or neutral as well as retardative, so far as instantaneous attraction while in the given positions is concerned. A wave starting in the Southern Ocean and moving north through the Atlantic for more than a day will run the whole gamut of positional relations to the moon and sun, and will, considered simply as an attached protuberance, be retardative, neutral, and accelerative in turn. In the case of waves that move to and fro across the water-bodies in seichelike fashion, it is obvious that the positional relations may be various. The most interesting cases are those of water-bodies whose periods of oscillation are nearly commensurate with the periods of the tidal forces. The breadth and depth of a water-body may be such that a wave started under the moon when it passes over the eastern margin will cross to the western side and return to the eastern just in time to fall under the moon's next crossing of the eastern margin, and so be reinforced by every return. In a body a little wider or a little shallower, the return of the wave would fall behind the moon's arrival and at its turn tend to retard the moon's motion, while in a body a little less wide or a little deeper the turn will come before the moon's arrival and the wave, at its turn, will tend to accelerate the moon's motion. But if either of these waves were to be followed through its whole course and its relations to the moon observed. it would be found to be accelerative, retardative, and neutral at different points.

Pursuing this line of inspection, it may be seen that the waves developed in the basins of the lithosphere must have a wide range of periods, some longer, many shorter, than the period of the tidal forces. Their rotatory influence on this basis of treatment is thus extremely difficult to analyse and evaluate, and the algebraic sum of all such influences is quite beyond mathematical determination.

The case is even more complicated when we consider amphidromic systems and those whose oscillations lie in lines oblique to the axis of rotation and to the moon's course. In the case of a stationary oscillation neither forward nor backward drag seems to be predicable as a total result, on this basis of treatment.

When all of the multitudinous phases are considered, it is clear that the case becomes so extremely complex that it can not be solved with any assurance of a reliable conclusion by analyzing the rotational effects of individual cases and summing the results. Some more basal method, so chosen as to escape these complications and the uncertainties of their interpretation, is required.

Poincaré, after a mathematical treatment of the influence of the watertides on the earth's rotation in the endeavor to simplify the case, reached the following conclusion:

L'influence des marées océaniennes sur la durée du jour est donc tout à fait minime et n'est nullement comparable à l'effet des marées dues à la viscosité et à l'élasticité de la partie solide du globe, effet sur lequel M. Darwin a insisté dans une série de Mémoires du plus haut intérêt.¹

### A MORE RADICAL MODE OF TREATMENT.

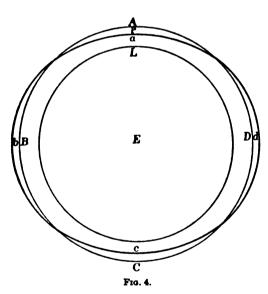
To the foregoing method of treating the rotational effects of the tides on the basis of the positions of the tidal protuberances and depressions. as such, there seem to be, as previously intimated, graver infelicities than those of mere complexity. The method appears to be defective in neglectng the cooperating effects of the changes of kinetic and potential energy that are associated with these differences in the distribution of matter. These protuberances are not fixed masses of matter, but rather aggregates of variations in the paths of the molecules of water in their revolutions about the earth's axis. In the production of these protuberances and depressions there are reciprocal increases and diminutions of the potential and kinetic energies of the water particles involved. In analyzing the influences of these on rotation, it will be serviceable to separate the factors of inertia and friction—including under the generic term friction all obstructive effects growing out of the relations of one particle to another—because the functions of these factors are contrasted, since the inertia tends to perpetuate any given state of motion, while the friction tends to reduce the amount of motion. There are also certain advantages in considering each particle separately as a body in revolution about the axis of rotation.

Let therefore the lithosphere be regarded as a perfect spheroid surrounded completely by an ocean of uniform depth, and let the matter of each particle be regarded as concentrated into a point and separated from its fellow particles by a complete vacuum, but let the collapse of the particles be prevented by a hypothetical force taking the place of the resistance to condensation which affects the water in nature. We shall then have an ocean made up of mass-points which move in perfect freedom from frictional and other obstructive relationships; in other words, these points will constitute satellites of the lithosphere which may here be regarded as a rigid body acting as a massive point at its center. The behavior of the mass-points may then be treated, qualifiedly, according to the principles of celestial dynamics. In fig. 4, let E represent the earth, the circle L the surface of the lithosphere, and the circle ABCD the ideal surface of the hydrospheric satellites when revolving without perturbation by the moon. Then, according to the principles of celestial mechanics, first applied to this class of cases by Newton, the orbit of a particle, p, will be a closed curve, abcd, closely resembling an ellipse, whose major axis is transverse to a line joining the centers of E and M. The general configuration, it will be noticed, is that of the "inverted tides." The particle p in passing

Bulletin Astronomique, vol. 20 (1903) "Sur un Théorème Général Relatif aux Marées,"
 par M. H. Poincaré, p. 223.
 Moulton's Celestial Mechanics, art. 156, p. 243.

from a to b will lose velocity—and hence kinetic energy—and gain potential energy. At the point b it will have the minimum of motion and the maximum of potential energy. From b to c it will fall back toward the center, a portion of its potential energy being converted into kinetic, and its velocity being increased and reaching a second maximum at c. In the second

M



half of its orbit, cda, similar exchanges of kinetic and potential energy will take place.

If p is affected by no friction or obstruction in its course, these exchanges of kinetic and potential energy will be compensatory and may be continued indefinitely without affecting the rotation of E. The case is that of an inner satellite or an inner planet when all the bodies involved are considered as rigid bodies or massive points. But if now friction be introduced at any point in the orbit of p, heat will be developed and dissipated, and energy lost to the system. Looked at in detail, it would seem that the retardation of p by friction on E in some phases of its orbit would be accelerative to E's rotation, and in other portions, retardative, for in some portions p's angular motion is greater than E's, and in others less, but traced out in its full history it appears that what is seemingly accelerative in one phase is retardative in another and that the ulterior effect is precisely measured by the loss of mechanical energy by conversion into radiant energy and dissipation. For example, friction between p and the normal periphery of E as represented

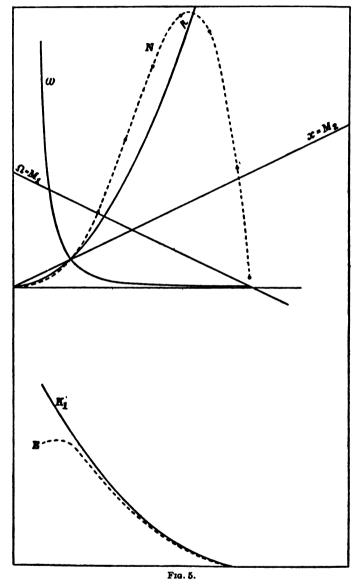
by ABCD, at or in the vicinity of c, will be accelerative in its immediate phase because p in this part of its orbit is moving faster than the contact portion of E, but the retardation of p in this portion will reduce the rise of p in the section at and near d which is retardative in its immediate phase because in this position p is moving more slowly than the normal

periphery ABCD. These would be precisely compensatory—outside action neglected—if there were no loss of energy by dissipation. This loss reduces the mechanical action of the system by precisely the mechanical equivalent of the heat lost.

In the actual system the distribution of the loss of energy is necessary to a complete solution. When the earth-moon tides alone are considered, it is clear that the lost energy must come either from the rotation of the earth or the revolution of the moon, or from both partitively. Now the moment of momentum of the system must remain constant and the distribution of the loss of energy must be such as to meet this requirement. Just what this distribution must be in a given case depends on the configuration of the system which then obtains, and is a question of celestial mechanics rather than of tidal theory. For the purposes of the present discussion it is of decisive moment to know whether the configuration of the earth-moon system at present is such that the earth and moon may recede with reduced rotation of the earth if the dominant phase of the tides is what has been called retardative, or may approach with accelerated rotation of the earth if the phase is what has been regarded as accelerative, or whether the configuration of the earth-moon system is such that it can move in one direction only when loss of energy by tidal friction takes place, bearing in mind that all tides give rise to friction and dissipation of energy. For a solution of this I appealed to Dr. Moulton, who found that, under the present astronomic relations of the earth and moon, any loss of energy by their interaction requires that the bodies recede from each other and that the rotation of the earth be diminished. This he finds to be rigorous under the laws of energy, and it seems to follow as a necessary inference that the special phase of the tidal action which caused the loss of energy is immaterial. While this determination at the time was wholly independent, it was soon recalled that Sir George Darwin had made a similar determination so far as the dynamic relations of the earth and moon under loss of energy are concerned. It does not appear, however, that he drew the inference we have just drawn, for this seems to exclude any differential effect dependent upon the positions or phases of the tides, other than such as is expressed in the amount of friction involved, which is dependent solely on the amount of the water-movement and not on its phase.

There are assignable configurations of the system in which a movement in the opposite direction would take place if energy were lost by interaction. Such a configuration would obtain if the centers of the earth and moon were within 9,000 miles of each other or their surfaces about 4,000 miles apart. The precise figure reached by Dr. Moulton, all computable influences being taken into account, is 9,241 miles. Dr. Lunn computed this independently, using slightly different values for some of the factors—essentially those of Darwin—and neglecting some inconsequential ones, and found the distance 9,113 miles. From this the conclusion seems inevitable that if, for any reason, the moon were separated from the earth within this distance, the tidal interaction of the earth and moon would tend to bring them together, an adverse tendency which the fission theory must face in addition to those cited before.

Relative to the question whether the lost energy, in the present configuration of the earth-moon system, must come wholly from the rotation of the earth or in part from the revolution of the moon, Dr. Moulton finds



that the loss would be derived partitively in the ratio of 27.3 from the rotation of the earth to 1 from the revolution of the moon.

<sup>&</sup>lt;sup>1</sup> The general relations here involved are shown graphically by Sir George Darwin in Thomson and Tait's Nat. Phil., II, p. 511. These are developed in much detail and with many applications in the paper of Dr. Moulton in this series, some of the details and appli-

Now, it being thus rigorously shown that the energy dissipated by the reaction between the tide-producing bodies must be taken from the mechanical energies possessed by the bodies, respectively, in the proportions given, and it being further shown that the evolution must take this direction and no other, it is clear that it will be possible to determine the effect of the water-tides on the earth's rotation if we can estimate the total energy dissipated by the tides, for the proper proportion of this can then be subtracted from the kinetic energy of the earth's rotation. We can of course use only imperfect data at present, but the uncertainties of these can be covered by allowances so as to approximate the true order of magnitude, and if the value does not prove to be a critical one, the order of magnitude may be as decisive for all geological purposes as a precise determination. If the value proves critical, the serial method may be applied to make the results cover the whole range of uncertainty. By thus dealing with the whole of the friction, and by applying it by means of the rigorous laws of energy, we not only avail ourselves of a radical mode of treatment but avoid the tangle of special interpretations and the discrepancies of tidal

Preparatory to an attempt to compute the total friction, it is worth while to note that an altogether exaggerated impression of the friction of the tides is inevitably conveyed by their association with wind-waves, river-currents, sea-currents, and other water-movements. As all of these. or nearly all of these, are the products of energy communicated to the earth by the sun's radiation, they may be assumed to be neutral in their rotational effects. If all these adventitious elements be removed in imagination, and the hydrosphere be made to take on a perfect calm, save as affected by the tidal forces, the picture of the frictional effects will be radically transformed, as may be seen by simple inspection. In the mid-ocean a water-particle will merely describe a circuit of a few feet in twelve hours, its movement on its fellow particles which are pursuing a somewhat similar circuit being almost imperceptibly slow; the movement on the bottom will be very slight. On a shore shelving at the rate of 1 foot in 50 feet, and with a tide of 5 feet, the edge of the tide would advance 250 feet in about 6 hours, or a little over 40 feet per hour. On the exceedingly low slope of 1 foot in 800 feet, the advance of a 5-foot tide would be only 666 feet There are of course concentrations of motion in bays, straits, per hour.

cations of which were worked out after this was written. In the accompanying graphic illustration by Dr. A. C. Lunn, the relations of the factors are somewhat differently arranged. In the upper diagram, fig. 5, the line " $\Omega=M_1$ " represents the angular velocity of the rotation of the earth; the line,  $\omega$ , the angular velocity of the moon in its orbit; r, the distance between the centers of the earth and moon; N, the relative days in the month;  $x=M_2$ , the orbital moment of momentum of the system. In the lower diagram, E represents the total energy of the earth-moon system;  $K_1$ , the kinetic energy of the earth's rotation.

The crossing of  $\Omega$  and  $\omega$ , where the angular velocity of the earth's rotation and the angular velocity of the moon's revolution are equal and they move as though a rigid body, is somewhat over 9,000 miles from the line of reference at the left. From this point of crossing to the left, where the distance of the centers is declining as shown by r, the total energy is declining as shown by E in the lower diagram and loss of energy promotes movement to the left. To the right of the crossing of  $\Omega$  and  $\omega$  the centers move apart, the total energy declines, and loss of energy promotes movement to the right.

and other special situations, that give quite notable movements, but the proportion of these to the whole is easily exaggerated. From a simple inspection of this kind it may be seen that the actual movement of the water, as distinguished from the wave-form, is of a low order and hence the friction is relatively small.

If one were to entertain the thought that the energy of movement of the tides arrested by the continents is a factor of much value in rotation, it should be recalled that the arrest of the easterly moving tides is to be set over against that of the westerly moving tides, and in the case of tides moving obliquely to the earth's axis there are easterly components to offset the westerly components. We have previously noted that the tides on the eastern sides of the Atlantic and Pacific average higher than those on the western side, so that, on the face of things, the balance of influence would, if the reasoning were fundamentally sound, favor rotational acceleration. But an analysis of the action shows that it results chiefly in a return wave, and this throws the problem back upon the dissipation of energy through friction. Some part of the energy of impact is not recovered in the return wave either through elastic resilience or the increased head which actuates the tidal ebb, but if the return wave is computed as though it were equal to the advance wave the loss will be covered.

Hough has made an important contribution to the frictional phase of the tidal problem by an investigation of the influence of viscosity on tidal waves and currents, in which he included stationary oscillations as well as progressive waves. He considered separately the tides whose wavelengths are large in comparison with the depth of the water-body and those in which the wave-lengths are small. If attention were confined to the main tidal phenomena, it might be thought that the wave-lengths small in comparison with the depth of water would have no representatives in tidal action, since the greatest depths of the sea are small compared with the amplitude of typical tidal waves, but, on consideration, it is apparent that these waves of great amplitude, by their various interactions upon one another, by the modifications which they suffer in their approaches to the shores, their arrests and their retreats, as also by their multitudinous interactions with wind-waves, sea-currents, etc., give rise to an indefinite number of waves of lesser amplitude, and that the length of these secondaries may be short compared with the oceanic depths. Hough did not consider the special effects of the irregularities of coasts and some other modifying conditions and these must be recalled in interpreting his extraordinary results. When these various agencies of modification are duly considered, it seems probable that after a very few days the original tidal oscillations largely lose their primitive amplitudes and take on shorter ones, and that in this way they pass beyond observation long before they actually die out.

Hough did not attempt to determine the complete destruction of the tidal waves by friction, but merely the time required for their reduction to the value represented by 1/e, or 0.368 of their original value. He found

<sup>&</sup>lt;sup>1</sup> Proc. Lond. Math. Soc., vol. 28, pp. 264-288.

that for waves of the class corresponding in his terminology to n=0, in waters of abysmal depths, the modulus of decay (to 0.368 value) is 42.6 years; for the class corresponding to n=1, 31.7 years; while for that corresponding to n=100, it is 4.8 years. The types, n=0, n=1, represent the longest and strongest waves; while those in which n has a high value represent waves of much shorter and feebler type and hence those first to be reduced to the limit named, as indicated by the moduli. In a case where the depth is 200 meters—the prevailing depth on the edge of the continental shelf—the moduli of decay for the types n=0 and n=1 are 4.5 and 3.3 years, respectively. For waves of 100 meters amplitude in water with a depth of 1 meter, the modulus of decay is about 80 minutes, bottom friction included. If there were no friction at the bottom, the modulus of decay would be about 2.25 years. In summation Hough says:

These results indicate how little can be the effects of viscosity upon the motion of the sea, except possibly in usually confined waters. It seems that wherever the depth exceeds a very moderate amount, say 100 fathoms, the rise and fall of the waters due to the sun and moon will not be appreciably affected by friction.

These determinations have a significant bearing upon the question how much of a given tidal wave is due to the force that has just been acting upon it during the current tidal period, and how much to the residual motion inherited from previous tides. If the motion of the waters when once generated requires these long periods for subsidence, it is obvious that each tidal wave may be perpetuated so as to cooperate with a long series of forcing actions in succeeding periods, if its period is commensurate with these. This supports the view, previously discussed, that the waves observed in those portions of the ocean most favorable for sympathetic accumulation are the products of a considerable series of forcing actions. This means that, at least in such cases, the element added with each tidal period is not measured by the actual waves observed, but by some minor fraction of it, and hence that the tidal friction which is daily exerted on the earth is by no means the amount necessary to reduce the observed tidal movement to zero, but merely that which is necessary to offset the daily increment, or its equivalent, the daily factor of decay. A wave of the type n=0 in water 200 meters deep, if commensurate action were perfect and dissipation, by giving rise to derivative waves, were wholly absent, would need to have less than  $\frac{1}{1600}$  of its value added to it daily to maintain its value. This must not be taken as representing an actual case, but it appears from considerations of this kind that the total energy of motion expressed by the tides daily is by no means a safe basis for estimating the energy lost through them. This must be computed directly from the water-movements under the conditions that actually affect them.

There is a check on carrying considerations of this kind too far, in the fact that the spring and neap tides and other special tides that depend on variations in the relations of the tide-producing bodies pass through their climacteric phases within one or two days of the astronomical configurations that give origin to them. They increase and die away with a relative

<sup>&</sup>lt;sup>1</sup> Loc. cit., p. 287.

promptness which shows that no tidal agency perpetuates its special effects in a special phase for a very long period.

There is a minor qualification of Hough's results that is worthy of passing notice. He took for his coefficient of viscosity 0.0178, which is one of the determinations for 0° C. The viscosity of water is much influenced by temperature. The coefficient for 17° C. is 0.0109. As this is about the average temperature of the surface of the earth, it may be taken as roughly, though not accurately, the average temperature of the ocean water. Salinity increases the viscosity. While I do not know of any direct determinations on sea-water, the determinations for normal solutions of sodium chloride imply that the viscosity of sea-water at 17° C. would be about 0.012, which makes Hough's results very conservative, so far as affected by the coefficient of viscosity used. This, however, is not so much the point as is the difference in the viscosity of the bottom and the surface water, respectively, in the low latitudes, that of the deep water being somewhere about 0.0195, while that of the surface in the tropics is about 0.0099, or but little more than half as great. This difference must increase relatively the motion of the water on itself and reduce that upon the bottom. It will thus substitute a distributive movement within the water, in which the friction is very low, for a more concentrated movement between the film of water attached to the bottom and that immediately above it, in which the friction is relatively high. The total effect is to reduce the frictional value.

Radical as are the suggestions of Hough's inquiry, a way to apply them directly, so as to secure a numerical expression of the total value of the friction of the tides in terms of work done, has not been found, and I have therefore tried to shape the problem so that it could be treated by the method of the engineer, as a given mass of water, with a given amount of flow, in a given time, under assigned conditions. To do this it seems necessary to substitute for the actual ocean an equal body of water in a more tractable form, but subject to equivalent friction. In doing this I have endeavored to give to the movements of the substitute ocean at least as great friction as that of the actual ocean. For the purposes of frictional treatment the ocean may be regarded as consisting of three portions, (a) the shallow water between the coast and the edge of the continental shelf, (b) the water on the slope between the edge of this shelf and deep water, and (c) the deep portion.

(a) The coast line is taken at 120,000 miles, which is nearly double the simple outlines of the ocean and about 5 times the earth's circumference. The depth of water on the outer edge of the continental shelf is taken at 600 feet, the accepted depth. The water is made to deepen uniformly from the coast to the edge of the shelf, which very greatly exaggerates its shallowness near the shore, where the friction is relatively greatest. The area is taken at 12,000,000 square miles, or 20 per cent more than Murray's estimate for this part of the actual ocean.

(b) The portion b is given a width of 50 miles, a descent from 600 to 9,000 feet, and an aggregate length of 120,000 miles. This length is much greater than the actual length of the continental margin, the excess being

intended to include a liberal allowance for the slope-tracts of the oceanic islands, which, however, are not subtracted from area c.

(c) The abysmal section is given a depth of only 9,000 feet and an area 20 per cent greater than that of the deep ocean, this reduction of depth and increase of area being intended to offset the frictional effects of the inequalities of the actual bottom.

The mean height of the tide in the substitute ocean is taken as 4.09 feet, which is equivalent to 4.9 feet for the actual ocean. The mean range of the tide for the 280 available stations given in Harris's table of tides harmonically analyzed is 4.548 feet. As these stations are chiefly in harbors where local concentration is felt, 4.548 feet is probably rather high for the average range of the tide, even on the coasts, and it is certainly much too high for the mean range over the whole ocean. In using the equivalent of 4.9 feet for the substitute tide in addition to the large allowances made above, it would appear that the computation is amply guarded against underestimation.

In using the foregoing guards against underestimation, which seem to me excessive, I have been somewhat influenced by the thought that there are derivatives from the observed tides which are not recognized and measured as such, but whose dissipation of energy should be covered by the computation. But, however well guarded, it is not presumed that any results now attainable will have much value beyond indicating the order of magnitude of the total friction. With the foregoing precautions the results should not be seriously less than the actual fact. But, if they are thought to be so by any one, the results can easily be multiplied accordingly.

With these data, a computation was made by Dr. W. D. MacMillan in the manner set forth by him in a following paper of this series, p. 71. This computation, it will be observed, was made for continuous motion, but in estimating the rate, 12.5 minutes between each lunar tide were allowed for the turn of the tide. He finds the yearly loss of energy to be  $38,918 \times 10^{14}$  foot-pounds. The rotational energy of the earth, reckoned on the assumption that the Laplacian law of density obtains, is  $157 \times 10^{27}$  foot-pounds. At the computed rate of loss, this amount of energy would last 40,440,000,000 years. The length of the day would be increased one second in about 460,000 years. In 100,000,000 years the total lengthening of the day would be about 3.6 minutes.

If this result does not wholly misrepresent the order of value of the friction of the water-tides, it follows that, even if the allowances for the irregularities of the tidal water-bodies be greatly increased, and if the formulæ of the engineers for the effects of friction be multiplied several times, and other allowances be made in the most generous manner, the effects of the water-tides on the rate of rotation of the earth during the known geological period are negligible. If the friction of the body-tides and the air-tides is also very small, there is no reason to expect to find in the geological evidences any appreciable deformations of the earth's body bearing the distinctive characteristics of tidal effects. On the other hand,

<sup>&</sup>lt;sup>1</sup> Rept. Coast and Geodetic Surv., 1900, pp. 664-677.

if the deductions which have heretofore been drawn from the older cosmogonic and geophysical conceptions are true, there should be geological testimony to support them. We turn therefore to the geological evidences with heightened interest.

### THE GEOLOGICAL EVIDENCES.

Perhaps the most important of the geological lines of approach to the rotational problem, is found in the evidences of an appropriate change or lack of change of the earth's form. At least it is this problematic change of form that gives the subject its obvious importance in diastrophism, to which this discussion is a preface. If the rotation of the earth were once appreciably faster than now, either the form of the lithosphere would have been more oblate than it is at present, or the surface-waters would have been accumulated at the equator by the increased centrifugal force, or both actions would have taken place conjointly; and a change from this configuration to the present one must have followed. If the lithosphere has changed its form appreciably within known geological times owing to reduction of rotation, such a change should be manifest in its structural deformations, especially in the deformations of the early ages. If the lithosphere has not essentially changed its form because of reduced rotation, but the waters served as the accommodating factor, this, if it were of sensible amount, should have been manifested by deposits of the kinds that imply prevalent and deep submergence in the equatorial regions and by erosions signifying prevalent and pronounced emergence in high latitudes in the former ages of higher rotation, and by the reverse in the later ages, both of which would be shown by the geological records of those regions.

## THE EVIDENCES FROM THE LITHOSPHERE.

The bearing of a possible change of form, assignable to a change of rotation, on terrestrial diastrophism has long been recognized in some measure by geologists, but the first attempt to reduce it to numerical terms seems to have been that made by President Van Hise several years ago.1 He inspired Prof. C. S. Slichter to make the computations necessary to show in numerical terms what would be the reduction in surface area if the rotation were changed to the degree postulated in Darwin's interpretation of the past history of the earth and moon. It was thought by him sufficient to base the computations on the convenient hypothesis of a homogeneous density. The change of surface area was shown to be large and this made it clear that, if such a change of rotation has taken place, it is an important factor in deformation. Even if the chief deformation took place early in the history of the earth, the effects should be apparent still in the inheritances of the regions most affected, and the record should show them. For the purpose of a more critical study of the subject, Professor Slichter has been kind enough to recompute for me the requisite data on the basis of a distribution of internal density as near that of the actual earth as our present knowledge permits. For this purpose Laplace's law

<sup>&</sup>lt;sup>1</sup> Van Hise, Jour. Geol., vol. 6, pp. 10-64, 1898; Slichter, ibid., vol. 6, pp. 65-68, 1898.

of increase of internal density was taken as perhaps the best expression of this factor and as being in fair accord with astronomical data. Professor Slichter extended the computation to other constants of the earth than those requisite for this inquiry and these give to his paper a value quite independent of its application to the present problem. His paper and table will be found on pages 61-67 of this volume.

Column 7 of this table (page 67) shows that ten periods of rotation have been selected, ranging from 3.82 hours to the present period. Darwin's hypothesis 1 leaves unassigned the precise period of rotation when separation took place, but from an inspection of the configuration of the spheroid at the rotation-period, 3.82 hours, and of the gravity in different parts of the spheroid at that stage, it seems safest to assume that a rotational period less than 3.82 hours would be necessary to cause fission. It seems best also to assume that at the 3.82-hour stage the earth was solid on the exterior, whatever may have been its internal condition. If this shall not seem so to any one, the arguments based upon the data of this rotational period can easily be shifted to the numerical values of the next period of 4.03 hours, or to any of the later periods given in the table.

From column 11 it will be seen that the equatorial circumference at the rotation-period, 3.82 hours, was 1,131 miles greater than it is at present, while the meridional circumference was 495 miles less. In changing to the present form, the tract immediately under the equator must have become shorter by 1,131 miles. The tracts under the parallels adjacent to the equator north and south would have become shorter by less amounts, those still farther away by still less amounts, until a little beyond 30° latitude, north and south, parallels are reached under which the crust would have theoretically remained unchanged so far as this immediate factor is concerned. These are the latitudes of mean radius for each stage of rotation and are shown in column 9. It will be noted that these shift from lat. 33° 20' to 35° 13' in the course of the series, but it is sufficient for our purpose to speak of the neutral zone as lying at 35° latitude, north and south respectively. The equatorial belt between these parallels, 70° in width roundly speaking, would therefore, by the postulated change, have become shorter along its central line by 1,131 miles, since the rotation-period of 3.82 hours. On its borders it would have suffered no change, and between the borders and the central line it would have suffered a graded series of shortenings.

That portion of the meridional circumference which lay within the equatorial belt should have been shortened in the course of the change from the rotation-period of 3.82 hours to that of the present, but the whole meridional circumference should have been lengthened 495 miles. It is obvious, therefore, that the areas north and south of the neutral zones must have become extended meridionally 495 miles plus the amount of the contraction in the equatorial zone, the precise value of which is unimportant here. It will be convenient to call these areas of expansion polar caps, though they reach down to about 35° latitude. In the course of the change named, the surface at the poles should have been raised and the curvature

<sup>&</sup>lt;sup>1</sup> The Tides, p. 360.

of the caps increased at all points. The extension should have been greatest at the poles and should have died away to zero at the parallel of no change. There was therefore a climacteric stretching at the poles and a climacteric compression at the equator.

Fig. 6 is intended to illustrate the nature of the change as seen from a point of view above one of the poles. To keep the view as true to perspective as practicable, the equatorial belt is foreshortened. The excess of area in the equatorial belt is represented by the black triangles, which are too small on account of this foreshortening. The deficiency of area in the polar region is represented by the white ground, which is more nearly in true proportion.

Changes in the crust of the earth of this magnitude, or of such lesser magnitude as would have followed a change from any of the other early periods of rotation to the present one, could scarcely have taken place

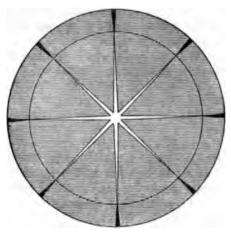


Fig. 6.—Polar projection of earth's hemisphere showing theoretical high-latitude tension and low-latitude compression involved in a change of rotation from 3.82 hours to present rate. Figure is drawn to true scale as seen from a point above pole, and in consequence the equatorial tract is foreshortened. The black triangles reduced in length by foreshortening show compression; the white show tension in essentially true proportions. The neutral line between areas of compression and of stretching lies at 33° 20′ latitude.

without leaving a record of themselves in the form of compressional and tensional phenomena. may, to be sure, suppose that the interior of the earth has always been sufficiently mobile, in one form or another, to permit inter-nal shift of material from areas of compression to areas of tension. and so to accommodate itself to the progressive change of form, but this can not reasonably be supposed to have taken place in the outer shell without having left evidences of itself, for this shell must be assumed to have been solid from an early state and, being at the surface, it was not under such pressure as to flow and hence must have been deformed in the familiar modes that characterize surface thrust and tension respectively. It is known from abundant geological

observation how the shell of the earth deports itself under conditions of compression and tension resulting from forces of the kind that would arise from the changes assigned. The data of Slichter's computations may therefore be interpreted by the usual methods.

The equatorial belt of the earth of the 3.82-hour rotation-period would differ from that of the present earth to the extent of a broad swell 180 miles high. In settling down this might doubtless relieve its excess of length in cross section by thrusting northward and southward into the areas of tension, but as its equatorial length was 1,131 miles greater than the present equator, it would seem that in an east-west direction the tract must fold, crumple, and overthrust on itself after the familiar fashion of

folded mountains. To estimate the result comparison may be made with estimates of the amount of crustal shortening involved in the formation of folded mountains. It is obvious that the estimates which assign the greatest amount of shortening to given amounts of folding are those which would give the least mountain production to the sinking of the equatorial belt in question and are hence the most conservative. One of the highest estimates of the crustal shortening involved in the formation of a familiar range of mountains, made by a competent geologist on the basis of much personal field work, is that of Professor Albrecht Heim for the formation of the Alps, which is 74 miles. Somewhat comparable estimates are those of Dr. Peter Lesley for the folds of the Appalachians west of Harrisburg, which is 40 miles, and that of Dr. G. M. Dawson for the Laramide Range in British Columbia, which is 25 miles. In the opinion of some other geologists these estimates are too high. If therefore we apply these to the equatorial belt the results will be relatively conservative. If we use Heim's figure, the sinking of the equatorial belt to the assigned amount should give 15 mountain ranges of the magnitude of the Alps standing across the equator. They should be short ranges dying away within 35° of latitude on either side. If we apply Lesley's estimate there should be 28 ranges of the order of the Pennsylvanian Appalachians standing across the equator; if the estimate of Dawson be used, there should be 45 ranges of the magnitude of the Laramides of British Columbia.

If we start with the 4.03-hour rotation-period instead of the 3.82-hour period, these figures become, 13, 25, and 40, respectively; and they may be easily reduced for later periods.

If, as an alternative, we choose to assign more mashing of the shell and less corrugation, it will merely give us a massive equatorial ridge with less cross-folding. If, as another alternative, we choose to assign more compression into denser rock, we shall have greater resistance to subsequent erosion and higher specific gravities to account for.

Under no tenable hypothesis, so far as I can see, can an equatorial protuberance of 180 miles comparable to the 3.82-hour period, or of 160 miles comparable to the 4.03 period, or of 87 miles comparable to the 5.35-hour period be assumed to have subsided to the present equatorial dimensions without having left a distinct record of itself in the form of transverse ranges of mountains, or of irregular protrusions, or of indurated terranes, or of some combination of these or of the other modes in which exceptional tangential stress is accustomed to express itself in the shell of the earth.

It is to be noted that, by the terms of the retardational hypothesis, the tangential stress must have been applied constantly from the beginning to the present time. It was indeed more rapidly applied in the earlier stages, but some stress has been added constantly ever since. If compression to a more compact form is to be assigned at all, in any important degree, it must be assigned to the first stages of stress, and the later protrusions would be all the more enduring on account of this early induration.

Now it is for every one to examine for himself the equatorial tract to see if it presents the character which the hypothesis requires. For myself, I am quite unable to find it. There is not even an equatorial belt of land,

much less an elevated girdle accidented by cross-folds, or knots, or contorted protuberances; nor do I find evidences of the truncated remains of these. Since the rotation-period of 15.63 hours, 40 miles of shortening should have been added to all that preceded, and 15 miles of this should have been added since the 19.77-hour period. Even if these were remote in years, they should have served to perpetuate a phenomenon that in its nature must have been dominant from the beginning, for it is difficult to assign any other agency of deformation that should have overmastered this, if it had this degree of efficiency. On the contrary, other agencies of deformation should, according to an accepted generalization derived from observation, have reënforced the deformation assigned to this cause, for old lines of yielding usually determine new ones.

As a matter of fact the depressions below sea level on the line of the equator are fully as great as the amount normal to a great circle; about three-fourths of the equatorial zone is submerged and one-fourth emergent. The oceans crossed are normally deep; the mountains of the tract are scarcely normal in height or massiveness, the Andes of Ecuador being the only conspicuous range within the equatorial tract. The mountains which cross the equatorial tract show no special signs of limitation to it, as they should if they were essentially dependent on the agencies involved in the retardational hypothesis.

If we take into consideration the whole compressional belt from 35° north to 35° south, it is found to embrace but little more than the average amount of land; indeed, the emergent surface within it is less, in proportion to the submerged area, than in the region north of it, though it is more than in the region south of it.

If we turn to the tensional areas that should, under the hypothesis of reduced rotation, lie between 35° north and south and the poles, the inspection is unembarrassed by any doubt about the effect of the stress upon the density of the rock, for appreciable stretching can not be assigned to rocks, except as it expresses itself by fissuring and equivalent modes, which leave an appropriate record. It is to be observed here again that, while the larger part of this tension was brought to bear in the early stages, it was, according to the hypothesis, continuous throughout the whole history. The results naturally assignable to this progressive tension would be a persistent fissuring and gaping radial from the poles, somewhat as implied by fig. 6. This must have run through all geological time, except as counteracted by some other agency. The cooling of the earth, or its shrinkage from internal molecular change or from any similar pervasive agency, would antagonize this, and if equal to it might prevent the actual opening of the fissures. But, to be consistent, this shrinkage must be applied generally and such application would intensify the difficulties in the equatorial belt in proportion as it relieved those of the polar caps. Simply to counteract the 495 miles of stretching required by the hypothesis in the rotational reduction from a period of 3.82 hours to the present, leaving out of consideration its special distribution, would require about 78 miles of vertical shrinkage in the polar regions and of 1,600 miles in the equatorial belt. But there is a special difficulty of distribution. The stretching required by

the hypothesis of rotational reduction is concentrated toward the poles, and hence, if tension is to be avoided in high latitudes, a very much larger radial contraction than the amount named must be postulated.

It must also be considered whether cooling, or any other similar contractional agency that can be postulated consistently with the early states of the earth assumed by this hypothesis, would be competent to offset the tensional effects imposed by the change of rotation in the polar regions.

If, to escape the difficulties arising from exceptional tension in high latitudes, it be assumed that the whole shell of the lower latitudes crowded toward the poles, this would involve meridional crowding and the formation of a system of folded ranges pointing to the poles, while east-and-west ranges should be absent proportionately, and thus the effects should be expressed in a distinctive manner. So it seems safe to conclude that, in one way or another, the high-latitude tension should have expressed itself in a characteristic way and, on account of its magnitude, its expression should be declared.

In comparing the facts with the theoretical requirements it must again be noted that the earlier formations should show the most evidence of tension, the Archean most of all. As a matter of fact, the Archean of high latitudes, as of low latitudes, shows abounding evidences of compression. It was my privilege in 1894, as geologist to the Peary Auxiliary Expedition, to see something of the ancient crystalline rocks of Greenland at They bore the same evidences of crumpling, latitudes as high as 77°. contortion, foliation, and thrust-stress generally as are commonly shown by the Archean rocks in lower latitudes. All descriptions of high-latitude formations of this age are identical in dynamic characters with those of lower latitudes, so far as my knowledge extends. The Archean terranes of Scandinavia and Finland lie far within the area of hypothetical tension, as do also those of Scotland and Canada, and even those of central Europe and the northern United States. The Archean and Proterozoic rocks of these regions bear evidences of tangential thrust of a most declared type, and no distinction between the most ancient rocks of the high-latitude and the low-latitude regions, in the matter of compressional characters, has, I believe, ever been detected. The literature of the subject does not show any special distribution of veins, dikes, normal faulting, and other evidences of tensional stresses correspondent to latitude. Apparently these features are essentially as prevalent in the equatorial belt as in the polar circles.

If the equatorial belt has been subjected from the beginning to constant increments of tangential stress and of gravity (column 4 of Slichter's table, page 67) while the polar regions have been concurrently subjected to increments of tension and decrements of gravity (column 5), it would seem that volcanic action would always have found adverse conditions in the former region and favorable ones in the latter, certainly so if pressure is adverse to liquefaction and if tensional faulting facilitates eruption. It does not appear, however, that volcanoes are in any appreciable degree infrequent in the tropical zone or that they are specially frequent in high latitudes. The prevailing impression is that they are somewhat more abundant in the tropics than in high latitudes, but there is little, if any, warrant for any latitudinal discrimination.

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The distribution of folded mountains appears to be quite indifferent to the latitudinal distinction which the hypothesis of rotational reduction involves. The great Cordilleran belt of the Americas begins far within the southern tensional area, is strong where it crosses the southern neutral belt, is also strong in the southern half of the equatorial belt, becomes weak, scattered, and tortuous in the northern half of this belt, attains strength and broadens as it crosses the northern neutral sone, and reaches great breadth and aggregate mass in the lower part of the north tensional area. About 30° within that zone, still strong, it swings about toward the Asian continent. The great tangled mass of mountains of central Asia lies chiefly in the northern tensional area. According to Suess, the thrust movement was generally from the northwest; that is, from the more highly tensional to the less highly tensional area. The great east-westerly range of southern Europe and Asia lies chiefly in the lower tensional and neutral zones and only at the east passes obliquely into the equatorial belt. A thrust from the compressional sone toward the tensional sone is indicated in the western portion and the opposite in the eastern portion. If, neglecting the latter, we fasten upon the former as dynamically probable under the hypothesis, it is to be noted that, with tension increasing in the direction of the thrust, it is not apparent whence came the resistance that was necessary to the intricate folding and distorting of the east-west ranges. Rather should we expect yielding in the direction of the tensional area and lateral crowding of the shell as it was pushed from the periphery toward the center of the tensional cap, with short meridienal ranges as the result. Without reviewing the multitude of minor mountains, it may be sufficient to note that the Urals, the ranges of Scandinavia and of the British Isles, the Appalachians, and the mountains of Greenland testify to the dominance of thrust phenomena in the northern zone of tension. Statistically considered, the facts now known give this northern zone precedence over all others in thrust phenomena. The great Archean tracts of Canada, Greenland, Scandinavia, and Finland carry the dominance of this thrust phenomena back to the earliest known ages. Taking the facts as we now know them, there seems to be no observational support for the compressionaltensional distribution which the hypothesis of great tidal retardation involves.

In the discussion thus far, agencies of compression and tension, other than rotational, have largely been ignored for the sake of following out, consecutively and uninterruptedly, the consequences of the hypothesis of rotational reduction and comparing them with observed facts. It is proper now to consider whether the intercurrence of other agencies of deformation would mask the results of tidal retardation, if these were of the order of magnitude implied by the fission theory of the origin of the moon, or even the close approximation of the moon to the earth in its early history under the planetesimal hypothesis. The existence of other causes of crustal deformation is of course fully recognized. To bring these under consideration in connection with the hypothetical tidal effects, it is necessary to note first their qualitative relations and second their relative values.

Essentially all of the other assignable causes of deformation of the major class seem to be general in their application and to affect all latitudes practically alike. This is true of cooling, of internal redistribution of heat, of molecular rearrangement, whether chemical, crystalline, or diffusive, of atomic transformations and decompositions, of radioactivity and presumably of igneous extravasations. Grant to these agencies whatever separate or combined effect may be their due, that effect, if it be general and essentially indifferent to latitude, as it seems that it must be, should be distinguishable from the effect of a superimposed agency that is pronouncedly correlated with latitude, because of this peculiarity. Granted a given amount of uniform earth shrinkage as the result of the general agencies named, or any of them, the crustal stress arising from this in the equatorial belt would be intensified by the addition of the stress of the same kind arising from the retardation of the earth's rotation, while the crustal stress which arises from these agencies in the polar regions would be proportionately relieved by the tension arising there from rotational retardation. A difference of result equal to the algebraic sum of the retardational and general stresses should be manifest in the resulting deformations. conspicuousness of this difference must depend largely on the relative values of the two classes of agencies, which is our second point of consideration.

If, on the tidal side, we take the higher deformative values given in Slichter's table (page 67), and if, on the other side, we take estimates of shrinkage made from a study of the foldings and faults of the earth, a comparison may be made. Quite without thought of this application, I have recently reviewed the data of the latter class in the endeavor to form a reasonable estimate of the amount of shrinking which the earth has probably undergone; and, while this estimate has little claim to value in itself, it may perhaps be taken to fairly represent the import of the present imperfect data. It is as follows:

If one is disposed to minimize the amount of folding, the estimate may perhaps be put roundly at 50 miles, on an entire circumference, for each of the great mountain-making periods. If, on the other hand, one is disposed to give the estimates a generous figure so as to put explanations to the severest test, he may perhaps fairly place the shortening at 100 miles, or even more. For the whole shortening since Cambrian times, perhaps twice these amounts might suffice, for while there have been several mountain-making periods, only three are perhaps entitled to be put in the first order, that at the close of the Paleosoie, that at the close of the Mesozoie, and that in the late Cenosoic. The shortening in the Proterozoic period was considerable, but is imperfectly known. The Archean rocks suffered great compression in their own times, and probably shared in that of all later periods, and if their shortening could be estimated closely, it might be taken as covering the whole. Assuming the circumferential shortening to have been 50 miles during a given great mountain-folding period, the appropriate radial shrinkage is 8 miles. For the more generous estimate of 100 miles, it is 16 miles. If these estimates be doubled for the whole of the Paleosoic and later eras, the radial shortening becomes 16 and 32 miles, respectively.\(^1\)

If we assign to the Proterosoic era a shrinkage equal to the Paleozoic, Mesozoic, and Cenozoic eras combined, and to the known Archean twice as much, the minimum and maximum estimates are 64 miles and 128 miles of radial shrinkage, respectively, or roundly 400 and 800 miles circumferential shortening, respectively.

<sup>&</sup>lt;sup>1</sup> Geology, vol. 1, Chamberlin and Salisbury, 1904, p. 551.

The assigned equatorial shrinkage from reduction of rotation since the 3.82-hour rotation-period is 180 miles, which is to be compared with the minimum 64 miles or the maximum 128 miles of the above estimate. Of course, it must be recognized that the 180 miles covers a period preceding the known Archean, which is not embraced in the latter figures; but if an allowance of two-thirds be made for this, the remaining 60 miles vertical shrinkage still bears a sufficiently large ratio to the stratigraphical estimates to make its effects certainly discernible, when the contrasted influences in polar and equatorial regions are brought into comparison.

The computation for maximum rotational change gives a meridional elongation of 495 miles; the stratigraphic estimate gives a meridional contraction of 400 and 800 miles minimum and maximum respectively. Allowing two-thirds of the 495 miles for the period preceding the known Archean, there remain 165 miles of elongation to reduce the effects of the 400 or 800 miles of contraction.

Combining equatorial and polar effects, the case stands 777 (400+377) vs. 235 (400-165), on the minimum basis, and 1,177 (800+377) vs. 635 (800-165), on the maximum basis, when two-thirds of the retardation is assigned to pre-Archean times. It would seem that differences of this order of magnitude should be clearly manifest in the phenomena.

#### THE EVIDENCE FROM THE HYDROSPHERE.

If there be any doubt about the practicability of detecting the influence of any great change in the rotation of the earth by the distinctive features of the deformation of its shell, we certainly have a very delicate means of detecting deformations in the position of the sea-level relative to the land. The position of the sea-level has been recorded by a series of shallow-water and shore deposits extending from the Cambrian period to the present, and this record was made with sufficient frequency and fidelity to answer every purpose of an inquiry of this kind. To a much greater extent than has usually been recognized, the known stratigraphic series is the product of shallow water, as shown by shallow-water life and appropriate physical evidences. In many cases some latitude must be allowed in the interpretation of these criteria of depth, but this can be the source of no essential error in a problem of deformation whose units are miles rather than feet; but, if required, a sufficient number of cases of irreproachable accuracy can be given, for at not a few geologic epochs there were emergences and submergences between which some stage of the transition marks the relations of the water surface to the land with positiveness and exactness. If, for instance, we know that in the critical regions, whether poleward or equatorward, a given horizon has been above the waterlevel and below the water-level respectively at two successive stages, we know that between these stages it was absolutely at the water-level. By means therefore of the successive emergences and submergences of given horizons, the relations of the sea to the land can be determined very accurately for a sufficient number of geological stages to be wholly decisive in such a problem as that in hand, and approximately for most of the other periods.

If the lithosphere could be supposed to have acted under the forces of gravity and rotation so nearly as though it were a perfect fluid that its form would be at all times perfectly adapted in all its parts to its rate of rotation, however much that may have changed, the argument here introduced would have little or no force. If this assumption is made here, it must of course be carried consistently throughout the whole range of deformative interpretation. If this is done faithfully, very grave difficulties will be encountered, so grave that, for myself, I have found them insuperable. It is indeed commonly thought consistent with experiments and geological observations, to regard the lithosphere as a solid which acts rigidly toward stresses of short period, and quasi-fluidly towards those of long period. Under this proposition it is possible to assume that the accommodation of the earth to a steady change of rotation might be so nearly perfect that variations would escape detection by even so delicate a registration as that of the sea-surface. But if this is done, it should be with the full consciousness that this is not a deduction from the proposition, but merely an assumption under it; for the general proposition that the lithosphere will yield under stress applied for a sufficient time does not in itself carry the conclusion that it will yield under the given stress in the given time. A quartz crystal is under self-gravitative stress and may have also been under terrestrial gravitative stress for eons, and yet it shows no signs of becoming a gravitative spheroid. Mountains and continents are under gravitative stresses and they probably yield to these, but at what rate is a practical question of much geological importance. The postulate of quasifluidal accommodation is not a solution; it is only a broad generalization under which a solution may be sought by specific evidence.

The shell of the earth is chiefly an aggregate of interlocking crystals which are possessed of specific elasticities of form, and the whole aggregate clearly has elasticity of form. If the great mass of the earth or even the deep outer portion be similarly an elastico-rigid solid, deformations will only take place when the stress-differences rise to equality with the elastic resistances, except in the limited form of strain, and to the limited degree permitted by the individual transfer of molecules from one rigid attachment to another. Deformations in this case await a certain accumulation of stress-difference. As the crux of the whole deformative problem lies largely in these basal conceptions, we may do well to turn to geological phenomena to ascertain, if possible, whether the earth does habitually yield concurrently with the accumulating stress-differences and thus constantly accommodate itself to stress-demands, or whether stress-differences do actually accumulate until the elastic limit is reached when deformation proceeds with relative rapidity until an approximate equilibrium is reached. This is but stating in dynamic terms the question of periodicity in geological deformation. On this question, a consensus of geological opinion can not now be cited without qualification. Apparently views differ and reserve predominates among cautious geologists. It appears to me, however, that strong evidence is steadily accumulating, from various quarters of the globe, that there were great periods of base-leveling of essentially world-wide prevalence, with concurrent sea-transgression, separated by briefer periods of deformation of similar prevalence. For these it does not appear that there will be found a consistent explanation except in the ability of the great body of the earth to accumulate stresses to a notable degree during the long periods of relative quiescence necessary for the base-leveling and the sea-transgression.

It would be going beyond the proper limit of this paper to try to establish this thesis by the citation of evidence, for this would involve a review of some large part of the great mass of stratigraphic, paleontologic, orogenic, and physiographic data possessed by geology. Suffice it therefore to note here that this is the one of the alternative views of the earth's deformative methods that seems at present best supported by geologic evidence. It is not wholly necessary to the following considerations, though it lends much strength to them.

Let it be assumed merely that the earth-body offers some appreciable resistance to deformation, an assumption which can scarcely be questioned, since the irregularities in the form of the geoid imply this, even when allowances are made for differences in the distribution of density. Let a limited slackening of the earth's rotation take place. This will disturb the preceding equilibrium between the centripetal and centrifugal forces and both the body of the earth and the water on its surface will experience stress-differences which give a tendency toward a new equilibrium. This equilibrium may be established by the subtraction of matter from the equatorial regions and its transfer to the polar regions internally or externally. The earthbody certainly offers some resistance to this transfer while the water on its surface offers practically no resistance at all because it is in circulation as the result of solar influence, and to effect the new distribution it is only necessary that it stop where the new demands of gravity require, and in this friction will lend its aid. The water surface may therefore be supposed to fall in the equatorial regions and rise in the polar regions until the new water surface of the globe conforms to the new equilibrium required. This must relieve, in some large part at least, the stress upon the body of the earth, for if the newly developed equilibrium required more matter in the polar regions the water would supply it, unless it were previously exhausted. Local stresses might remain where the land was left protuberant, but geological evidence shows that such protuberances can be maintained for long periods by the effective rigidity of the earth, if they do not exceed a certain measure. Such a protuberance of the equatorial land may be treated as any other local protrusion of the earth's body. therefore, in the case in hand, an equatorial mass became protuberant above the surface of the geoid sufficiently to overcome the effective rigidity of the part of the earth affected, the appropriate deformation would follow.

The determination of what mass is sufficient for such deformation is qualified by the available time. Given infinite time and the requisite mass would doubtless be relatively small in a body like the earth, even on the hypothesis of elastic rigidity; for, even within the limit of elasticity, deformations may take place by the transfer of molecules from one rigid attachment to another individually. But whatever might be the results if indefinite time were available, the practical case is one of limited time and,

as implied above, geological evidences seem to show that stresses do accumulate to certain large magnitudes before sensible deformations take place. Meanwhile surface transfers by wind and water action are in progress. The protuberant equatorial belt postulated must ever have been shedding material northward and southward, mechanically and by solution, thus building up sedimentary series in the flanking sea-borders. tuberant tendency was ever renewed by slackening rotation, this should have become a perpetual process and, as we have seen, should have been a pronounced factor, if not the dominant one, in the earth's deformation, if the reduction in rotation was as great as the hypothesis of earth-moon fission requires. It appears, therefore, that an annular latitudinal distribution of the sediments and of the lands derived from the sediments should have arisen, and this should have cooperated with the tendency of the waters to polar accumulation in giving a distinctive configuration to the distribution of land and water. Yet, as a matter of fact, the surface configuration is singularly free from latitudinal sones. There is a very rough tendency toward a meridional arrangement, but the essential fact is that the arrangement is irregular. The protuberances and depressions consist of an unsymmetrical interspersion of independent triangular, quadrangular, oval, and scarcely definable areas.

Going more into detail, and in this insisting only on the obvious general proposition that the water-level in the equatorial sone should have tended to a low position relative to the land and to a high position in the polar regions, we may note that the Greenland Archean embossment not only stands high above the water-level to-day but is singularly free from evidences of submergence in the past. At various periods from the Cambrian onwards, the water-level has stood low about its base and has risen above and fallen below the present shore-line. Much the same may be said of the great Archean tract of Labrador and of the region west of Hudson's Bay, as also of that of Scandinavia and Finland. It is a remarkable fact, in the light of the matter in hand, that the old lands which are now best exposed, the lands that seem to have been longest out of water, and that have been most persistently above sea-level, are more largely the lands of high latitude than of low latitude.

A candid and critical survey of the relations of land and water in high and low latitudes alike, and in all longitudes, especially in the northern hemisphere where best known, and where the protuberant lands furnish the best record, seems to me to reveal a singular constancy of relations, subject only to oscillations measured by a few thousands of feet at most, an order of magnitude quite out of harmony with any hypothesis which, to cite a very conservative example, requires that the equatorial tract should have been 8 miles higher than at present when the rotation-period of 14 hours prevailed.

If the moon were once much nearer the earth than now the tides should have been much stronger and the littoral deposits of the early ages should show not only greater coarseness but greater vertical range. Geologists have not been generally convinced that the earlier sediments are different in any such systematic way from those of later times.

#### MINOR EVIDENCES.

If the earth's rotation were much more rapid than now in early times, the gyratory component affecting the courses of the winds would have been strengthened and probably trees would have required a corresponding strengthening of the trunks, branches, and roots to meet this successfully. Such provisions are not certainly detectable. In the coal-accumulating eras trees grew to great heights without tap roots, and in some cases they appear to have grown on accumulations of vegetal débris which could not have furnished a very secure hold, and yet there is no evidence that they were especially subject to overthrow. In no way is it clear that the life of the early ages, either vegetal or animal, was adapted to atmospheric movements essentially different from those of to-day.

A more rapid rotation should have caused a stronger deflection of the streams to the right hand in the northern hemisphere and to the left in the southern. This should have resulted in tilted aggradation planes. However, these might not now be capable of detection, even if present.

It is probable that some changes would arise from the shortness of the day and night, but it is not clear just what these would be nor what would be the criteria for their detection.

It seems safe to say, in summation, that no geological evidence of any unquestionable kind, or even probable kind, is found that supports the theoretical postulate of a former high rate of rotation of the earth.

The geological criteria are not delicate enough, however, to forbid the belief that the rotation of the earth has changed in some minor degree during the time over which the record extends. If the deformative effects of such changes were small compared with those of the other diastrophic agencies, they might be so far masked as to escape ready detection.

### ACCELERATIVE AGENCIES.

There are some agencies, apparently not very potent ones, which tend to accelerate the earth's rotation and to offset the influences of the tides. Of these the most familiar is the shrinking of the earth. It was noted in the review of the hypothesis of Darwin that in the initial stage the shrinkage of the earth was made more effective rotationally than the tides of the sun. It was of course assumed as a basis for this that the loss of heat at that stage was quite exceptionally great. The computations of Woodward 1 and others have shown that the present rotational effects of loss of heat, assuming the correctness of current estimates, is exceedingly small. Even if the estimates of loss of heat need to be increased, as seems probable, such loss can not be a very efficient agency. Shrinkage from other sources, as molecular rearrangement, atomic reconstruction, or other agencies, may have a more considerable effect. The rotational results of the contraction of the body of the earth from a radius of 4,160 miles to 3,960 miles, with intervening stages, as computed by Dr. MacMillan on the assumption that the Laplacian law of density is maintained, are as follows:

<sup>1 &</sup>quot;The effects of secular cooling and meteoric dust on the length of the terrestrial day." <Astro. Jour., No. 502, 1901: "From this it appears safe to conclude that the length of the day will not change, or has not changed, as the case may be, by so much as a half second in the first ten million years after the initial epoch." p. 174.

Length of day for various lengths of earth's radius-Laplacian law of density.

Radius of earth (miles).	increase (miles).	Length of day.		
3,960		24 h 0 m 0 s		
3,970	10	24 7 17		
3.980	20	24 14 35		
3.990	30	24 21 54		
4,000	40	24 29 14		
4.010	50	24 36 36		
4,020	60	24 43 58		
4,040	80	24 58 46		
4.060	100	25 13 39		
4,060 4,110	150	25 51 10		
4,160	200	26 29 08		

If current views of the shrinkage of the lithosphere founded on the folds of the shell and on overthrust faulting are valid, its accelerative effects on the earth's rotation are greater than the retardative effects of its water-tides as hereinbefore computed, and perhaps greater than all the tides combined.

It is possible that the earth may respond to the radiant energy of the sun as a thermal engine and that its rotation may be influenced by this, but the subject is obscure and elusive, if not delusive, and no attempt will be made to develop it here.

If, as seems probable, the evening sky, because of clouds, dust, etc., offers more resistance than the morning sky to the passage of solar radiation tangential to the earth, there is a slight preponderance of light-pressure in favor of acceleration of rotation, but it must be very small.

### CONCLUSION.

The application of the most radical and the most rigorous method of estimating the frictional value of the present water-tides, a method which brings to bear practically all the friction of these tides as a retardative agency, irrespective of their positions or directions of motion, seems to show that they have only a negligible effect on the earth's rotation.

From the best available evidence I conclude that the tides of the lithosphere are chiefly elastic strains and have little retardative value, while the tides of the atmosphere are too small to be measured.

The accelerative influences seem to be also negligible, so far as geological applications are concerned.

In close accord with these deductions, the geological evidences indicate that there has been no such change in the rate of the earth's rotation during its known history as to require it to be seriously considered in the study of the earth's deformations.

I desire to acknowledge my great obligations to my colleagues, C. S. Slichter, F. R. Moulton, A. C. Lunn, and W. D. MacMillan, for the indispensable aid which their several contributions have rendered to these studies and for criticisms and suggestions relative to my own paper.



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## THE ROTATION-PERIOD OF A HETEROGENEOUS SPHEROID

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### THE ROTATION-PERIOD OF A HETEROGENEOUS SPHEROID.

It is a simple problem to determine the rotation-period of an ellipsoid of revolution, if it be postulated that the density of the body is uniform, and that the form is that assumed by a perfect liquid under like conditions of rotation. A table of the rotation-periods of such a body having the same volume and mean density as that of the earth, computed for various values of the eccentricity of an elliptic meridian section, will be found on p. 327 of Part II of Thomson and Tait's Natural Philosophy (edition of 1890). It is the purpose of the present investigation to obtain analogous results for an ellipsoid of variable density, assuming a law of increasing density from surface to center approximate to that actually possessed by the present earth. The law of density assumed in the computation is the well-known law of Laplace:

 $\rho = Q \frac{\sin q \, a}{a} \tag{1}$ 

in which the symbols have the meaning given on page 64. According to this law the internal layers or shells of equal density gradually change from the shape of the surface to forms more and more nearly spherical as the center of the spheroid is approached. The forms of these layers are best expressed in the case of ellipsoids of revolution by the ellipticity of a meridional section. This number is computed by subtracting the length of the polar or short axis from the length of the equatorial or long axis and dividing the result by the length of the equatorial axis.\(^1\) The variation in the value of the ellipticities is shown by the dotted line in fig. 7. In this diagram the polar axis is represented as divided into ten equal parts. The ellipticities of the shells of equal density are expressed as percentages of the ellipticity of the surface. Thus the ellipticity of the shell that cuts the polar axis at 0.5 of the distance from the center to the surface is equal to 85 per cent of the surface ellipticity, while the ellipticity of the central shell is about 80 per cent of the surface ellipticity.

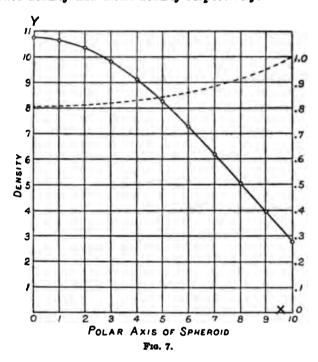
If we assume a surface density of 2.75 and a mean density of 5.50, the above expression takes the form:

$$\rho = \frac{4.365 \, a_0}{a} \sin \frac{2.4605 \, a}{a_0} \tag{2}$$

The variation in density according to this law is shown graphically by the continuous curve of fig. 7.

<sup>&</sup>lt;sup>1</sup>The mean axis or the polar axis is often used as the divisor. There is little difference in the results for the small values of the ellipticity usually involved.

An inspection of the diagram shows that the density increases quite uniformly for a considerable distance as we pass from the surface toward the center. We finally come to a central nucleus of nearly uniform density. The density at the center, required by the Laplacian law, is 10.74. This value would be modified if values different from 2.75 and 5.50 be assumed for the surface density and mean density respectively.



LIST OF SYMBOLS USED, WITH MEANING.

 $a_0 = \text{mean radius of surface of spheroid.}$ 

a =mean radius of any homogeneous shell in interior of spheroid.

b = equatorial radius of any homogeneous internal shell of spheroid of revolution.

 $b_0$  = equatorial radius of surface of spheroid.

c = polar radius of any internal homogeneous shell of spheroid.

 $c_0$  = polar radius of surface of spheroid.

Q = a constant = 4.365 for earth-spheroid.

q = a constant = 2.4605 for earth-spheroid.

 $\rho$  = density of any homogeneous shell of mean radius a.

 $\rho_0$  = surface density of spheroid = 2.75.

 $a_e$  = equatorial attraction or value of gravity at equator of any spheroid.

 $a_p$  = polar attraction or value of gravity at pole of any spheroid.

m=ratio of centrifugal force at equator to gravity at equator.

e = eccentricity of any homogeneous internal shell of spheroid.  $c_0$  = eccentricity of surface of spheroid.

 $\varepsilon = \frac{b-c}{b}$  = ellipticity of any homogeneous internal shell of spheroid.

 $\epsilon_{\bullet}$  = ellipticity of surface of spheroid.

M = centripetal acceleration at equator of spheroid.

While the Laplacian law of density originated in an assumption of Laplace which had little to recommend it beyond mere plausibility, the law is now believed to be fairly close to the truth. The computed values of the earth's precession based upon this law of density agree well with the observed values. The law is probably quite as near to the truth as is the measured value of the earth's mean density, which must enter as a basal number into any formula of density we may adopt.

The plan of the investigation is substantially as follows: The attraction of the heterogeneous spheroid of given ellipticity is first found for points on the equator and at the poles of the spheroid. These results are substituted in Clairaut's well-known equation connecting gravity at the pole and at the equator with the equatorial centripetal acceleration, and hence with the rotation-period of the earth. In this manner the rotation-period for any given ellipticity of meridional section becomes known.

Clairaut himself gave expression to formulas which give the attraction at external points of any rotating liquid ellipsoid. For polar and equatorial points these may be written as follows (referring to the preceding list for the meaning of the symbols):

Equatorial attraction 
$$\equiv a_{\bullet} = \frac{4}{3} \cdot \frac{\pi}{b_{\bullet}^2} K \left\{ \int_{0}^{a_{\bullet}} \rho da^3 + \frac{3}{5} \cdot \frac{1}{b_{\bullet}^2} \int_{0}^{a_{\bullet}} \rho d(a^3 \epsilon) \right\}$$
 (3)

Polar attraction 
$$\equiv a_p = \frac{4}{3} \cdot \frac{\pi}{c_0} K \left\{ \int_0^{a_0} \rho da^3 - \frac{6}{5} \cdot \frac{1}{c_0^2} \int_0^{a_0} \rho d(a^5 \epsilon) \right\}$$
 (4)

In both formulas K is a constant whose value depends upon the units of measure in which the various magnitudes are expressed.

These expressions assume that each stratum of density  $\rho$  has the ellipticity  $\epsilon$  that would exist for the given rotation-period if all strata were perfectly liquid. In other words, the formula is built upon the hypothesis of the perfect fluidity of the spheroid. If we apply these expressions to the present earth we assume that the rigidity of the earth is not sufficient to withstand for geological intervals of time the stresses that would exist if the form of its surface differed materially from that of a free liquid.

The above expressions (3) and (4) can not be integrated until we substitute for  $\rho$  the appropriate law of density from (1) above. Using the notation:

$$\varphi(a) \equiv \frac{Q}{q^2} \left( \sin q a_{\bullet} - q a_{\bullet} \cos q a_{\bullet} \right) \tag{5}$$

<sup>&</sup>lt;sup>1</sup> See "History of the theories of attraction and the figure of the earth," by I. Todhunter, London, 1873, vol. 1, p. 220.

we may obtain

$$\int_{0}^{a_{0}} \rho d(a^{5}\varepsilon) = 5a_{0}^{2}(\varepsilon_{0} - \frac{m}{2})\varphi(a_{0}) \qquad \int_{0}^{a_{0}} \rho da^{5} = 3\varphi(a_{0}) \qquad (6), (7)$$

from which we obtain

$$a_{s} = \frac{4\pi}{b_{0}^{2}} K \varphi(a_{0}) \left( 1 + \frac{a_{0}^{2}}{b_{0}^{2}} \left[ \epsilon_{0} - \frac{m}{2} \right] \right)$$
 (8)

$$a_{p} = \frac{4\pi}{c_{0}^{2}} K\varphi(a_{0}) \left(1 - \frac{2a_{0}^{2}}{c_{0}^{2}} \left[\epsilon_{0} - \frac{m}{2}\right]\right)$$
 (9)

The relation between m and  $\epsilon_0$  depends upon the "degree of heterogeneity" of the earth: that is, it depends on the departure of the surface and central density from the mean density. For a homogeneous earth we may write, as is well known:

$$2\epsilon_{\bullet} = \frac{5}{2} m \tag{10}$$

but for a body possessing the law of heterogeneity given by equation (2) above, we can deduce the expression 1

$$2\epsilon_{\bullet} = \frac{5}{2.536} m \tag{11}$$

The change of the denominator of the fraction on the right-hand side of the equation from 2 to 2.536 is brought about by the change of hypothesis from

to the hypothesis

pothesis
$$B...... \begin{cases}
Central density = 10.74 \\
Mean density = 5.50 \\
Surface density = 2.75
\end{cases}$$

If we further assume that the mean attraction at the surface of the earth is 982 dynes per gram of attracted matter, we may write the equations of equatorial and polar attractions in the simple form

$$a_{\bullet} = 982 \ (1 - 0.1739 \epsilon_{0}) \tag{12}$$

$$a_{\bullet} = 982 \ (1 - 0.1739 \epsilon_{0})$$
 (12)  
 $a_{p} = 982 \ (1 + 0.3477 \epsilon_{0})$  (13)  
 $M = 982 \ (1.0144) \epsilon_{0}$  (14)

$$M = 982 \ (1.0144)\varepsilon_0 \tag{14}$$

It is upon the numerical values here written that the results of the following table have been obtained. The results can be checked by substituting for  $\varepsilon$  in equations (3) and (4) the expression

$$\varepsilon = [0.09645 (a^2 + a^3) + 0.8071] \varepsilon_0 \tag{15}$$

which is an algebraic function approximately equivalent to the transcendental relation between  $\varepsilon$  and a, within the interval with which we are

<sup>&</sup>lt;sup>1</sup> See a "Treatise on attractions, Laplace's functions, and the figure of the earth," by John H. Pratt, London, 1871, p. 116.

concerned. This expression was found in 1898 by Mr. H. C. Wolff, then a graduate student at the University of Wisconsin.

Investigations concerning the properties of the spheroid have usually hypothecated an ellipsoid so nearly spherical that small error would be introduced by neglecting the square of the ellipticity in comparison with its first power. Such has been done in the present instance. For that reason it is hardly possible to extend the computations to spheroids of greater ellipticity than those given in the table. As a matter of fact, the writer believes that he has extended the computations as far backward as is practicable without straining the approximate formulas beyond their limit of significance.

The Rotation-period of a Heterogeneous Spheroid.

			· · · · · · · · · · · · · · · · · · ·			<u> </u>			
(1)	(	2)	(3)	(4)	(5)	(6)	(7)	(8)	
Polar radius (mean radius = unity).	(mear	atorial dius 1 radius nity).	Ellipticity.	Equatorial attraction	Polar attractio	at equator	Rotation- period of hetero- geneous spheroids	Rotation- period of homo- geneous spheroids	
	1			(dynes).	(dynes)	. (dynes).	(hours).	(hours).	
С		b	ε <sub>o</sub>	a,	ap	M	T	T	
0.997726	1.0	001137	0.003411	981.4	983.1	3.398	23.934	23,934	
.9967		0017	.005	981.0	983.5	4.98	19.77	22.21	
.9947		0027	.008	980.6	984.7	7.97	15.63	<b></b>	
.9933		0033	.010	980.2	985.4	7.96	14.00		
.9867		0067	.020	978.6	988.8	19.92	9.91	10.94	
.9767		0117	.035	976.1	993.8	34.86	7.51		
.9667		0167	.05	973.6	999.6	49.8	6.30		
.9600		0200	.06	971.6	1002.0	59.8	5.76		
.9533		)233	.07	970.1	1006.0	69.7	5.35		
.9428		0286	.0859	967.2	1011.0	85.5	4.84	5.49	
.9333		)333	.10	964.9	1016.0	99.6	4.49		
.9267		0367	.11	963.1	1020.0	109.6	4.29		
.9167		<b>1417</b>	.125	960.5	1025.0	124.5	4.03		
.9065	1.0	<b>)467</b>	.1402	958.1	1030.0	139.7	3.82	4.37	
(9)	(9) (10)		(11	)	(12)		(13)		
) '			' '	Equatorial contrac-		• •			
Latitude of	mean	Equate	orial contrac-	Equatorial		Meridional elor	ign-   metici	onal elonga- tion	
radius. (per cent).		(mile		(per cent).	(I	niles).			
35° 13	 3/		0.0000	00 0.00			00		
35 1		ł	0.06	15		0.05		12	
			0.16	4		0.12	l	30	
35		l	0.21	52		0.16	[	40	
35		1	0.55	137		0.32	- 1	80	
34 47	47 1.03		256		0.53	j	132		
34 3			386		0.76	1	190		
34 2			468		0.90	ı	225		
34 16			550		1.06	- 1	265		
34 5 2.73		680		1.30		325			
	33 53 3.21		799		1.48		370		
33 4		ł	3.54	881		1.60		400	
33 3	33 33 4.04			1006		1.80		450	
33 20	0		4.54	1131	l	1.98	1	495	

CONTRIBUTIONS TO COSMOGONY AND THE FUNDAMENTAL PROBLEMS OF GEOLOGY

# ON THE LOSS OF ENERGY BY FRICTION OF THE TIDES

BY
WILLIAM D. MACMILLAN

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### ON THE LOSS OF ENERGY BY FRICTION OF THE TIDES.

In this paper the waters of the ocean will be conceived as concentrated in a basin, rectangular in shape, the width of which will be taken as 2,860 miles and the length as 60,000 miles. The bottom will have a uniform slope from the surface to a depth of 600 feet at 100 miles from the shore, dropping then to a depth of 9,000 feet at a distance of 150 miles from the shore, and then parallel to the surface out to the middle of the basin, the opposite side having the same shape. The tide will be supposed to rise  $4\frac{1}{11}$  feet in 6 hours—falling at the same rate.

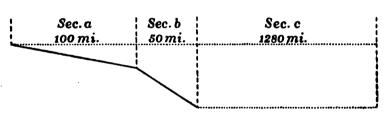


Fig. 8. Cross-section of basin (showing one-half).

The rigorous determination of the motion of the water in such a basin on the principles of hydrodynamics seems to be unattainable at the present time. It is true that, to start with, we have the equations of motion of a viscous incompressible liquid, but I have not succeeded in finding a solution for them with the assigned boundary conditions, and therefore am not able to give an exact statement of the rate at which energy is dissipated. We may, however, approach the problem through some of the formulæ of hydraulics and obtain an approximation, which, even though it be rough, will permit us to form some idea of the order of magnitude of dissipation. If we liken the ebb and flow of the tide to the flow of water in a canal we can use the formulæ of engineers for the loss of head due to friction and viscosity, and consequently the loss of energy.

Weisbach 1 gives us the following formula:

$$h = \xi \times \text{length} \times \frac{(\text{mean vel.})^2}{2g} \times \frac{\text{wetted perimeter}}{\text{area of cross-section}}$$

where h is the total fall of water in the canal necessary to maintain the flow,  $\xi$  is the coefficient of friction, and g is the acceleration of gravity. We will

<sup>&</sup>lt;sup>2</sup> Theoretical Mechanics. Translated by E. B. Coxe. 8th Amer. ed., sec. 475.

take g=32 feet per second per second. The coefficient  $\xi$  itself is dependent upon the velocity. As a result of many experiments the following value is assigned:

$$\xi = 0.007409 \left( 1 + \frac{.1920}{v} \right)$$

where v is the mean velocity. From this formula it will be observed that  $\xi$  increases as the velocity decreases.

This formula is applicable to a canal in which the cross-section is uniform throughout its length. In order to adapt it to a canal of variable cross-section and velocity an integration is necessary. Consider an element of the canal between parallel cross-sections at distances l and l+dl from the upper end, and put

$$v =$$
velocity  $a =$ area of cross-section  $p =$ wetted perimeter

We have then, from the above formula,

$$\frac{dh}{dl} = \xi \frac{v^2 p}{2ga}$$

or, since 2g = 64 and

$$\xi = .007409 \left( 1 + \frac{.1920}{v} \right)$$

this may be written

$$\frac{dh}{dl} = \frac{.007409}{64}(v^2 + .1920v)\frac{p}{a}$$

This expression represents the slope at the point l necessary to maintain the flow. The rate of fall of the water in this element of the canal is obtained by multiplying the slope by the velocity, that is

$$v\frac{dh}{dl}$$
 = rate of fall of the water

The distance through which the water falls multiplied by its weight gives the amount of work done expressed in foot-pounds. Consequently

$$E = \int_{l_1}^{l_2} wv \frac{dh}{dl}$$

where E is the amount of work done per unit time and w is the weight of water in the element considered. The volume of water is equal to adl and the weight of a cubic foot of water is approximately 62.3 pounds. Therefore

$$w = 62.3 \ adl$$

These values substituted in the expression for E give

$$E = \frac{62.3 \times .007409}{64} \int_{l_1}^{l_2} (v^2 + .1920v^2) \ pdl$$

Consider now a section of the basin 1 foot wide, and by means of this formula compute the loss of energy in this strip in one second of time with such a tide as has been supposed.

Let us begin with section "a." We will suppose the surface of the water is level throughout the section. A tide of  $4\frac{1}{11}$  feet in 6 hours means a constant flow throughout the section of 600 feet per hour or one-sixth foot per second, i.e.,  $v=\frac{1}{6}$ . The wetted perimeter is the bottom only, that is p=1, and this also is constant throughout the section. We have, therefore,

$$E_a = \frac{62.3 \times 0.007409}{64} \int_{0.007409}^{0.0000} \left[ \left( \frac{1}{6} \right)^3 + 0.1920 \left( \frac{1}{6} \right)^2 \right] dl$$

where  $E_a$  is the work done in section "a", the length of the strip being 528,000 feet. Evaluating the above expression there results

 $E_a = 37.939$  foot-pounds per second

The flow in section "a" shows that the surface sinks at the rate of  $\frac{1}{5250}$  foot per second. We will suppose that the surface of section "b" sinks at the same rate, remaining always level. If l be measured from the beginning of the section the velocity at the distance l is given by  $v = \frac{q}{a}$ , when q is the volume of water flowing by the point l and a is the area of the cross-section. Since the surface sinks  $\frac{q}{5250}$  foot per second

$$q = 100 + \frac{l}{5280} \qquad a = 600 + \frac{7l}{220}$$

Therefore

$$v = \frac{1}{6} \times \frac{528000 + l}{528000 + 28000 + 28000}$$

The wetted perimeter is constant throughout the strip, so that p=1. The length of the strip is 50 miles, or 264,000 feet. The dissipation of energy in this strip is then

$$E_b = \frac{62.3 \times 0.007409}{64} \int_0^{284000} \left\{ \frac{1}{6^2} \left[ \frac{528000 + l}{528000 + 28l} \right]^2 + \frac{0.1920}{6^2} \left[ \frac{528000 + l}{528000 + 28l} \right]^2 \right\} dl$$

By putting l = 264000x this expression becomes

$$E_b = \frac{62.3 \times 0.007409 \times 264000}{64 \times 216} \int_0^1 \left\{ \left[ \frac{2+x}{2+28x} \right]^2 + 1.152 \left[ \frac{2+x}{2+28x} \right]^2 \right\} dx$$

which may also be written

$$E_{b} = \frac{62.3 \times 0.007409 \times 264000}{512 \times 216 \times 14^{3}} \int_{0}^{1} \left\{ \left[ 1 + \frac{27}{1 + 14x} \right]^{2} + 32.256 \left[ 1 + \frac{27}{1 + 14x} \right]^{2} \right\} dx$$

From the reduction of this expression is obtained

 $E_b = 1.124$  foot-pounds per second.

Making the same assumptions with respect to this section that were made with respect to section "b", we find in the formula  $v = \frac{q}{a}$ 

$$q = 150 + \frac{l}{5280} \qquad a = 9000$$

so that

$$v = \frac{792,000 + l}{9000 \times 5280}$$

As before, we take p=1. The length of the section is 1,280 miles, or 1,280  $\times$  5,280 feet. If now we put  $l=5280\times1280x$ , the expression for the lost energy is

$$E_{\bullet} = \frac{62.3 \times 0.007409 \times 5280 \times 1280}{900^{2} \times 64} \int_{0}^{1} \left\{ (15 + 128x)^{2} + 172.8 (15 + 128x)^{2} \right\} dx$$

which reduces to

 $E_o = 142.484$  foot-pounds per second

Combining these results, we have

$$E_a = 37.939$$
  $E_b = 1.124$   $E_o = 142.484$  Total, 181.547

The total work done in the entire strip is therefore 181.547 foot-pounds per second. If the work done on the opposite shore of the basin be the same, the total work done per linear foot of basin is 363.094 foot-pounds per second. In a basin 60,000 miles long this would amount to  $11,503 \times 10^7$  foot-pounds per second, or  $36,300 \times 10^{14}$  foot-pounds per year of  $365\frac{1}{4}$  days.

The kinetic energy of the earth due to its rotation is given by the formula  $T = \frac{1}{2}I\omega^2$ 

where T is the kinetic energy, I is the moment of inertia of the earth, and  $\omega$  is its angular velocity. The moment of inertia depends upon the law of density of the earth's interior which is not known. We will probably be not far astray in using the Laplacian law of density, *i.e.*,

$$S = G \frac{\sin m \frac{r}{a}}{\frac{r}{a}}$$

<sup>\*</sup> See Tisserand, Méc. Cél., 2, p. 234.

where S is the density at the distance r from the center, a is the earth's radius, and

$$m=141^{\circ} 40' 28'' \equiv 2.4727$$
  $G=4.426$ 

With the Laplacian law of density, then

$$I = \frac{2}{3}Ga^{4} \int_{0}^{a} \int_{0}^{2\pi} \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} \left(\frac{r}{a}\right)^{3} \sin m \left(\frac{r}{a}\right) \cos \varphi d\varphi d\theta d \left(\frac{r}{a}\right)$$

$$= \frac{8}{3}\pi Ga^{4} \int_{0}^{a} \left(\frac{r}{a}\right)^{3} \sin m \frac{r}{a} d \left(\frac{r}{a}\right)$$

$$= \frac{8}{3}\pi a^{4} \frac{G}{m^{4}} [(3m^{2} - 6) \sin m - (m^{3} - 6m) \cos m]$$

With the same law of density the mass of the earth (M) is

$$M = Ga^{2} \int_{0}^{a} \int_{0}^{2\pi} \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} \left(\frac{r}{a}\right) \sin m \frac{r}{a} \cos \varphi d\varphi d\theta d\left(\frac{r}{a}\right)$$

$$= 4\pi Ga^{2} \int_{0}^{a} \frac{r}{a} \sin m \frac{r}{a} d\left(\frac{r}{a}\right)$$

$$= 4\pi a^{2} \frac{G}{m^{2}} [\sin m - m \cos m]$$

Consequently, by the division of these two expressions,

$$I = \frac{2}{3m^2} \left[ \frac{(3m^2 - 6)\sin m - (m^2 - 6m)\cos m}{\sin m - m\cos m} \right] Ma^2$$

Substituting in this the numerical value of m, there results

$$I = .335 Ma^2$$

and therefore

$$T = .168 Ma^2\omega^2$$

Taking the radius of the earth at 3,958 miles, its mean density at 5.5, and the sidereal day as 86,164 seconds, it becomes

$$T = 159 \times 10^{27}$$
 foot-pounds

At the rate of loss due to tidal friction as calculated above, this amount of energy would last  $43,900\times10^6$  years. The day would be lengthened by 1 second in about 500,000 years.

### CONTRIBUTIONS TO COSMOGONY AND THE FUNDAMENTAL PROBLEMS OF GEOLOGY

# ON CERTAIN RELATIONS AMONG THE POSSIBLE CHANGES IN THE MOTIONS OF MUTUALLY ATTRACTING SPHERES WHEN DISTURBED BY TIDAL INTERACTIONS

BY
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### ON CERTAIN RELATIONS AMONG THE POSSIBLE CHANGES IN THE MOTIONS OF MUTUALLY ATTRACTING SPHERES WHEN DISTURBED BY TIDAL INTERACTIONS.

### I. INTRODUCTION.

Sir George Darwin has written a number of classical memoirs on the subject of tidal friction which are remarkable not only for the profundity and the thoroughness of the mathematical analysis, but also for the charm and lucidity of the exposition of the nature of the problems treated, the hypotheses upon which the investigations were based, and the conclusions which were reached. Frequent references will be made to these memoirs in this paper, and for simplicity they will be designated by numbers as follows:

1. On the bodily tides of viscous and semi-elastic spheroids, and on the ocean tides upon a yielding nucleus. < Phil. Trans. of the Royal Soc., Part I, 1879, pp. 1-35.

2. On the precession of a viscous spheroid, and on the remote history of the earth.

Trans., Part II, 1879, pp. 447-538.

3. On the secular changes in the elements of the orbit of a satellite revolving about a

tidally distorted planet. <Phil. Trans., Part II, 1880, pp. 713-891.

4. On the tidal friction of a planet attended by several satellites, and on the evolution of the solar system. <Phil. Trans., Part II, 1881, pp. 491-535.

5. The determination of the secular effects of tidal friction by a graphical method. <Pro-

ceedings of the Royal Society of London, vol. 29 (1879), pp. 168-181.

Darwin's method of treatment is to express the tide-generating potential as a sum of terms, each of which is the product of a second-order solid harmonic and a simple time harmonic, and then to derive the corresponding surface harmonics which define the tidal deformations when the system has assumed a condition of steady movement. The results are adapted to viscous or elastico-viscous spheroids, the heights and lags of the several tides being expressed in terms of the speeds of the tides and the viscosity, or the rate of decay of elasticity of the tidally distorted body. The effects of these tides upon the motions of the disturbed and disturbing bodies are then derived with rare skill.

Apparently Darwin's work can be questioned, if at all, only where he applies his analysis to the earth-moon system. Here he reaches the conclusion that very probably the moon once separated from the earth by fission, and that it has been driven to its present distance by tidal friction. In reading these conclusions we should heed his warning:1

The result at which I now arrive affords a warning that every conclusion must always be read along with the postulates on which it is based.

It is quite evident from Darwin's discussions that he accepts, as a general basis for reasoning on the problems of cosmogony, the Laplacian nebular hypothesis with its implication of a one-time fluid earth; indeed, in 2, p. 536, line 3, and in 4, p. 530, first paragraph, he explicitly states that he adopts this hypothesis in its main outlines. It is obvious that this point of view might tend to give one a confidence, perhaps without his realizing fully the postulates upon which it was based, that, even if the spherical harmonic analysis should not be strictly applicable to a heterogeneous earth whose liquid parts are broken up by continental masses, it still would be sensibly correct when applied to a fluid body such as the earth was supposed, according to this theory, to have been in the past. It is now known that there are very grave, and I believe fatal, objections to the Laplacian ring theory. At any rate, one would not now make it a postulate in a discussion involving so many and such serious complexities as arise in the theory of tidal evolution, or allow it seriously to influence his conclusion as to what is the most probable of the various possible hypotheses. Darwin examined with great thoroughness the character of the results for various conditions of viscosity and semi-elasticity, and only where he undertook to say what seemed to him the most probable of various possible series of events was he influenced, possibly, by his preconceptions as to the early condition of the earth. To illustrate the delicacy of the discussion we shall enumerate a few of his conclusions together with the hypotheses upon which they were based.

In 3, Part IV, and in its summary, pp. 871-876, Darwin discussed the inclination of the moon's orbit and the obliquity of the ecliptic. Considering first the hypothesis of small viscosity and tracing back the system until the day and month were equal, he found that, if this hypothesis is true, the lunar orbit and the earth's equator must initially have had considerable mutual inclination. "If this were necessarily the case, it would be difficult to believe that the moon is a portion of the primeval planet detached by rapid rotation, or by other causes." (3, p. 873.) Then taking up the hypothesis of large viscosity and supposing that it was "large enough," he found, tracing the system back, that when the day and month were of equal length, then the lunar orbit was sensibly in the plane of the earth's equator, which was inclined 11° or 12° to the plane of the ecliptic. His final conclusion from this discussion (pp. 875-876) was that it will be most nearly correct to suppose that the earth in the earliest times, though plastic, possessed a high degree of stiffness, and that now the greater part if not the whole of tidal friction is due to oceanic tides, and not to bodily tides, for in this way the theory of the fission of the parent mass into two bodies and the present inclination can be best reconciled.

In 3, Parts V and VI, the effects of tidal friction upon the eccentricity of the lunar orbit were considered. The equations were integrated on the hypothesis of small viscosity, and it was found that in past times the eccentricity was much smaller than at present, nearly vanishing when the day and month were equal. If it had been assumed that the viscosity was very large, the eccentricity of the lunar orbit would have been the greater the farther back the system was traced. Since a large original eccentricity

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is incompatible with the fission hypothesis, it is found necessary to conclude that, at least for a part of the earth-moon history, the viscosity of the part of the earth distorted by tides has been small. Hence that viscosity which best explains the inclination of the lunar orbit causes trouble when considering its eccentricity. Since numerical details were not worked out in the discussion of the eccentricity for large viscosities, it is not known to what quantitative extent the two things are antagonistic, and it may very well be that a viscosity could be assumed which would explain largely the inclination and not be particularly unfavorable to the eccentricity. There were so many partial contradictions and so much uncertainty that Darwin attempted to draw no final conclusion from this discussion (3, p. 879).

Another question, still more critical, is the distance from the earth to the moon when the day and month were of equal length. In 2, section 18, neglecting part of the action of the sun, Darwin found that the day and month were equal at 5<sup>h</sup> 36<sup>m</sup>, corresponding to a distance between the centers of the earth and moon of 10,000 miles. In 3, section 22, including all the action of the sun, he found that the initial period and distance were less. The numerical results were not obtained, but he stated (3, section 22, p. 835):

It is probable that an accurate solution of our problem would differ considerably from that found in "Precession" (5<sup>h</sup> 36<sup>m</sup>), and the common angular velocity of the two bodies might be very great.

In the summary of this same paper, p. 877, he said:

In section 22 it [the sun's action] is only so far considered as to show that when there is identity of periods of revolution of the moon and earth, the angular velocity must be much greater than that given by the solution in section 18 of "Precession."

Computations given at the end of the present paper, section 14, show that the difference is actually unimportant.

Apparently, in order to make this fission hypothesis workable it must be shown that if the day and month ever were equal they had such a period that the distance from the earth to the moon was much less than 10,000 miles.

There are many places where it would be easy for a careless reader of Darwin's work to lose the connection between the conclusions and the hypotheses upon which they were based. For example, taking approximately that viscosity which would produce the most rapid tidal evolution, he found ' that 57,000,000 years ago the day was 6 45 long, and that the length of the month was 1.58 of our present days. Notwithstanding the fact that this is quite a different thing from having proved that the earth-moon system has actually gone through this series of changes, undoubtedly many first-hand and more second-hand readers of Darwin's work have supposed that this computation gives a fairly certain and definite account of the evolution of these bodies. But it is interesting to find in the same memoir, section 14, under the hypothesis that the observed secular acceleration of the moon's mean motion is due entirely to tidal friction, and also that the earth is purely viscous, the conclusion that the length of the month is now being increased at the rate of only 2 20 in

<sup>&</sup>lt;sup>1</sup> 2, Section 15, Table IV, and pp. 529-531.

100,000,000 years. Very different results were obtained by assuming that the earth is elastico-viscous. Under this assumption in 700,000,000 years the day will be about as long as at present, the month nearly a day shorter than at present, and the obliquity of the ecliptic about 5° less than it is now. The discussion of the secular acceleration of the moon was closed with these remarks (2, p. 483, last paragraph):

The conclusion to be drawn from all these calculations is that, at the present time, the bodily tides in the earth, except perhaps the fortnightly tide, must be exceedingly small in amount; that it is utterly uncertain how much of the observed 4" of acceleration of the moon's motion must be referred to the moon itself, and how much to the tidal friction, and accordingly that it is equally uncertain at what rate the day is at present being lengthened.

Notwithstanding these uncertainties, in the general discussion at the end of the final paper of the series (4, pp. 532-533) Darwin states:

The previous papers were principally directed to the case of the earth and moon, and it was there found that the primitive condition of those bodies was as follows: The earth was rotating, with a period from two to four hours, about an axis inclined at 11° or 12° to the normal to the ecliptic, and the moon was revolving, nearly in contact with the earth, in a circular orbit coincident with the earth's equator, and with a periodic time only slightly exceeding that of the earth's rotation.

Then it was proved that lunar and solar tidal friction would reduce the system from this primitive condition down to the state which now exists by causing a retardation of terrestrial rotation, an increase of lunar period, an increase of obliquity of ecliptic, an increase of eccentricity of lunar orbit .

It was also found that the friction of the tides raised by the earth in the moon would explain the present motion of the moon about her axis, both as regards the identity of the axial and orbital revolutions, and as regards the direction of her polar axis.

Thus the theory that tidal friction has been the ruling power in the evolution of the

earth and moon completely coordinates the present moting power in two bodies, and leads us back to an initial state when the moon first had a separate existence as a satellite.

This initial configuration of the two bodies is such that we are almost compelled to believe that the moon is a portion of the primitive earth detached by rapid rotation or other causes.

The problem of tidal evolution is an extremely complicated one and the uncertain factors which enter into it are very many. Darwin's treatment of it as a mathematical problem was masterly and worthy in every respect of the highest admiration. He was generally very cautious in drawing conclusions with respect to the actual earth-moon system. The danger lies in the formidable and protracted analyses coming in between the hypotheses and the conclusions, which might lead one to suppose that results drawn from a particular set of postulates necessarily belong to the earth and moon, particularly if they, in a general way, coincided with his preconceptions of cosmogony. Even though Darwin may have been without fault in this respect, it is not certain that less critical minds, especially if they were without the illuminating experience of finding by actual computation how great changes in the results would be produced by admissible changes in the hypotheses, would not attach undue importance to some particular computation. There is nothing deduced from observations so far made or from Darwin's investigations that would prevent one, if it suited his fancy, from drawing the conclusion that the motions of the earth and moon have been for 100,000,000 years about as they are at present.

In questions of cosmogony, where immense intervals of time are involved, the problem of tidal evolution is obviously one of great importance, unless it shall some time be shown that it is not a sensibly efficient factor. The two most obvious methods of determining its efficiency are by direct attacks from the mathematical standpoint, or by comparing its certain implications with as many facts given by observation as possible. The first is mainly the method of Darwin, and he has written what will certainly always be an extremely important chapter in the question when considered in the broadest possible way. His results can be improved, apparently, only by a determination of the physical properties of the earth as a whole, and by an estimate of the loss of energy in the ocean tides. While there is hope for the former from seismic vibrations, certain astronomical phenomena, and the character of the crustal deformations as revealed by geological studies, the results are not now so well established that they do not need support from other sources. The second method, that of comparing the positive implications of the tidal theory with observed facts in as extended a way as possible, is broadly speaking that adopted in this paper. Since there can be no test of time-results except on the basis of other doubtful hypotheses, and since it is impossible to draw any certain conclusions in the questions involving the time, this variable has been entirely eliminated from the discussion except in section 14. In a general way it may be said that the energy of the system has been taken as the independent variable, for it is known that under any sort of friction it must degenerate into heat. The results are characterized by certainty so far as they go, but as compared with Darwin's they are in most cases much less explicit as to particulars. The discussion is mostly attached to the fundamental equations of moment of momentum and energy. After the work was well advanced it was found that Darwin had applied fundamentally the same methods to illustrate his results in a paper supplementary to his main series and published in a different serial (No. 5 in the list previously given). The variables he used were different from those employed here, but, though for certain purposes they may be more convenient, nevertheless, for the sake of complete independence, those originally selected have been retained.

When the discussion is based simply upon the moment of momentum and energy equations, the number of quantities to be determined is greater than the number of the determining equations. To attain the greatest simplicity the general problem has been divided up into a number of special cases covering altogether the entire field. In this way each special problem is very easily understood and the question as a whole is much illuminated.

#### GENERAL EQUATIONS.

The problem treated will be that of the tidal interactions of  $m_1$  and  $m_2$ , which, in certain cases, are supposed to be disturbed by a large distant mass S. The masses  $m_1$  and  $m_2$  will be assumed to be spherical. Then let

 $a_1 = \text{radius of } m_1$ ;  $a_2 = \text{radius of } m_2$ 

r = distance from the center of  $m_1$  to the center of  $m_2$ 

-r =distance from  $m_1$  to center of gravity of  $m_1$  and  $m_2$  $\overline{m_1+m_2}$ 

 $m_1$  $\rho_2 = \frac{1}{m_1 + m_2}$ -r =distance from  $m_2$  to center of gravity of  $m_1$  and  $m_2$ 

x, y, z = set of fixed axes with origin at center of gravity of  $m_1$  and  $m_2$ 

i—inclination of orbits of  $m_1$  and  $m_2$  to xy-plane

 $i_1$  = inclination of plane of equator of  $m_1$  to xy-plane  $i_2$  = inclination of plane of equator of  $m_2$  to xy-plane

e = eccentricity of relative orbit of  $m_1$  and  $m_2$ 

 $a = \text{major semi-axis of relative orbit of } m_1 \text{ and } m_2$ 

 $\theta$  = angular velocity of revolution of  $m_1$  and  $m_2$ 

 $P = \frac{\pm 2\pi}{av.\theta} = \text{period of revolution of } m_1 \text{ and } m_2$ 

 $\omega_1$  = angular velocity of rotation of  $m_1$ 

 $\omega_2$  = angular velocity of rotation of  $m_2$ 

 $D_1 = \frac{\pm 2\pi}{\pi}$  - period of rotation of  $m_1$ 

 $D_1 = \frac{\omega_1}{\omega_1}$   $D_2 = \frac{\pm 2\pi}{\omega_1}$  = period of rotation of  $m_2$  $\omega_2$  S = a distant disturbing mass

r' - distance of S from center of gravity of  $m_1$  and  $m_2$ 

P' = period of revolution of S

M, M', M'' = whole moment of momentum of system, exclusive of S, about the z, x, and y-axes respectively

E = whole energy, both kinetic and potential, of system exclu-

The moment of momentum of  $m_1$  about the z-axis is the moment of momentum about its axis of rotation multiplied by  $\cos i_1$  plus its moment of momentum of revolution around the z-axis. The rotational moment of momentum of  $m_1$  around an axis through its center and parallel to the e-axis is

$$c_1m_1a_1^2\omega_1\cos i_1$$

where c<sub>1</sub> is a constant depending upon the law of density. The corresponding quantity for  $m_2$  is

$$c_2m_2a_2^2\omega_2\cos i_2$$

The moment of momentum of revolution of  $m_1$  about the z-axis is

$$m_1 \rho_1^2 \theta \cos i = \frac{m_1 m_2^2}{(m_1 + m_2)^2} r^2 \theta \cos i$$

and the corresponding quantity for  $m_n$  is

$$m_2 \rho_2^2 \theta \cos i = \frac{m_2 m_1^2}{(m_1 + m_2)^2} r^2 \theta \cos i$$

Therefore the total moment of momentum about the 2-axis is

$$M = \frac{m_1 m_2}{m_1 + m_2} r^2 \theta \cos i + c_1 m_1 a_1^2 \omega_1 \cos i_1 + c_2 m_2 a_2^2 \omega_2 \cos i_2$$
 (1)

The whole energy of the system is the kinetic energies of rotation, plus the kinetic energies of revolution, plus the potential energy.

The kinetic energy of rotation of  $m_1$  is  $\frac{1}{2}c_1m_1a_1^2\omega_1^2$ , and there is a similar expression for the kinetic energy of rotation of  $m_2$ . The kinetic energy of revolution of  $m_1$  is

$$\frac{1}{2} m_1 \rho_1^2 \theta^2 + \frac{1}{2} m_1 \left(\frac{d\rho_1}{dt}\right)^2 = \frac{1}{2} m_1 \left(\frac{m_2}{m_1 + m_2}\right)^2 r^2 \theta^2 + \frac{1}{2} m_1 \left(\frac{m_2}{m_1 + m_2}\right)^2 \left(\frac{dr}{dt}\right)^2$$

and there is a similar expression for the kinetic energy of revolution m.

The potential energy of the system is  $-\frac{k^2m_1m_2}{r}$ , where  $k^2$  is the gravitation constant.

Therefore the total energy is

$$E = \frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} r^2 \theta^2 + \frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} \left(\frac{dr}{dt}\right)^2 - \frac{k^2 m_1 m_2}{r} + \frac{1}{2} c_1 m_1 a_1^2 \omega_1^2 + \frac{1}{2} c_2 m_2 a_2^2 \omega_2^2$$
 (2)

From the two-body problem we have

$$r^2\theta = \pm k \sqrt{(m_1 + m_2) a (1 - e^2)}$$
 (3)

the determination of the ambiguous sign depending upon the direction of revolution, and

$$r^2\theta^2 + \left(\frac{dr}{dt}\right)^2 = k^2 (m_1 + m_2) \left(\frac{2}{r} - \frac{1}{a}\right)$$
 (4)

$$P = \frac{2\pi a^{\frac{\alpha}{3}}}{k\sqrt{m_1 + m_2}} \tag{5}$$

By means of (3), (4), and (5) equations (1) and (2) reduce to

$$M = \frac{+m_1 m_2 k^{\frac{1}{2}} P^{\frac{1}{2}}}{(2\pi)^{\frac{1}{2}} (m_1 + m_2)^{\frac{1}{2}}} \sqrt{1 - e^2} \cos i + \frac{2\pi c_1 m_1 a_1^2 \cos i_1}{D_1} + \frac{2\pi c_2 m_2 a_2^2 \cos i_2}{D_2}$$
 (6)

$$\frac{E}{\pi} = \frac{-m_1 m_2 k^{\frac{1}{2}}}{(2\pi)^{\frac{1}{2}} (m_1 + m_2)^{\frac{1}{2}} P^{\frac{1}{2}}} + \frac{2\pi c_1 m_1 a_1^2}{D_1^2} + \frac{2\pi c_2 m_2 a_2^2}{D_2^2}$$
(7)

the sign of  $P^{1}$  depending upon the direction of revolution, and the signs of  $D_1$  and  $D_2$  upon the directions of rotation of  $m_1$  and  $m_2$  respectively.

The units are so far arbitrary. We shall choose them so that

unit of time = mean solar day
$$2\pi c_1 a_1^2 = 1$$

$$\frac{m_1 m_2 k^2}{(2\pi)^{\frac{1}{2}} (m_1 + m_2)^{\frac{1}{2}}} = 1$$
(8)

Then equations (6) and (7) become

$$M = P^{\frac{1}{2}} \sqrt{1 - e^2} \cos i + \frac{m_1 \cos i_1}{D_1} + \frac{c_2}{c_1} \left(\frac{a_2}{a_1}\right)^2 \frac{m_2 \cos i_2}{D_2}$$
 (9)

$$\frac{E}{\pi} = -\frac{1}{P^{\frac{3}{2}}} + \frac{m_1}{D_1^2} + \frac{c_2}{c_1} \left(\frac{a_2}{a_1}\right)^2 \frac{m_2}{D_2^2} \tag{10}$$

If we represent the ascending nodes of the planes of the orbit and of the equators of  $m_1$  and  $m_2$  by  $\Omega$ ,  $\Omega_1$ , and  $\Omega_2$  respectively, the moment of momentum equations for the x and y-axes are similarly

$$M' = P^{\frac{1}{2}} \sqrt{1 - e^{2}} \sin i \sin \Omega + \frac{m_{1} \sin i_{1} \sin \Omega_{1}}{D_{1}} + \frac{c_{2}}{c_{1}} \left(\frac{a_{2}}{a_{1}}\right)^{2} \frac{m_{2} \sin i_{2} \sin \Omega_{2}}{D_{3}}$$

$$M'' = P^{\frac{1}{2}} \sqrt{1 - e^{2}} \sin i \cos \Omega + \frac{m_{1} \sin i_{1} \cos \Omega_{1}}{D_{1}} + \frac{c_{2}}{c_{1}} \left(\frac{a_{2}}{a_{1}}\right)^{2} \frac{m_{2} \sin i_{2} \cos \Omega_{2}}{D_{3}}$$

$$(9')$$

#### III. THE LAPLACIAN LAW OF DENSITY.

In treating the rotations of such bodies as the earth it is not permissible to regard them as homogeneous, for in the case of the earth the density of the surface rock averages about 2.75, while the average density of the whole earth is 5.53. If we let  $\sigma$  represent the density of the sphere m, the well-known expression for it suggested by Laplace is

$$\sigma = \frac{G \sin \left(\mu \frac{r}{a}\right)}{\frac{r}{a}} \tag{11}$$

where r is the distance from the center of m, and where G and  $\mu$  are constants depending upon the constitution of the body. According to this law the density of the body increases from the surface to the center, and is finite at both the surface and the center. We shall determine G and  $\mu$  by making both the surface density and the mean density agree with the results furnished by observation.

The mass is found from the equation

$$m = 4\pi \int_{0}^{a} \sigma r^{2} dr = 4\pi a^{2} G \int_{0}^{a} \frac{r}{a} \sin \left(\mu \frac{r}{a}\right) d \frac{r}{a} = \frac{4\pi a^{2} G}{\mu^{2}} [\sin \mu - \mu \cos \mu]$$
 (12)

Let  $\sigma^{(a)}$  represent the surface density and  $\bar{\sigma}$  the mean density. Then G and  $\mu$  are determined by the equations

$$\sigma^{(0)} = G \sin \mu \qquad \bar{\sigma}\mu^2 = 3G \left[ \sin \mu - \mu \cos \mu \right] \tag{13}$$

The density at the center is

$$\sigma^{(o)} = G\mu \tag{14}$$

In the case of the earth  $\sigma_1^{(\phi)}=2.75, \bar{\sigma}_1=5.53$ , whence it is found from (13) and (14) that

$$G = 4.39633$$
  $\mu = 2.46579$   $\sigma_1^{(o)} = 10.840$  (15)

In our ignorance as to the density of the surface material of the moon,  $m_2$ , we shall assume that for it  $\mu_2 = \mu$  and determine  $G_2$  from (12) so that  $81.7m_2 = m_1$ . We find, taking  $a_1 = 3.958.2$  miles and  $a_2 = 1.081.5$  miles, that

$$G_2 = 2.6393$$
 (16)

whence

$$\bar{\sigma}_2 = 3.32$$
  $\sigma_2^{(0)} = 1.65$   $\sigma_2^{(0)} = 6.51$  (17)

# IV. MOMENT OF INERTIA FOR THE LAPLACIAN LAW OF DENSITY.

Letting I represent the moment of inertia of the sphere m, we have

$$I = \int r^2 \cos^2 \varphi \, dm = \int_0^{2\pi} \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} \int_0^a \sigma \, r^4 \cos^3 \varphi \, dr \, d\varphi \, d\theta \qquad (18)$$

Substituting the expression for  $\sigma$  from (11) and integrating, we find,

$$I = \frac{8\pi a^5 G}{3\mu^4} [3 (\mu^2 - 2) \sin \mu - \mu (\mu^2 - 6) \cos \mu]$$
 (19)

or, making use of (12),

$$I = \frac{2a^2m \left[3 (\mu^2 - 2) \sin \mu - \mu (\mu^2 - 6) \cos \mu\right]}{3\mu^2 \sin \mu - \mu \cos \mu}$$
 (20)

Hence the values of  $c_1$  and  $c_2$ , occurring in (1), are determined by equations of the form

$$c = \frac{2}{3\mu^2} \frac{\left[3 \left(\mu^2 - 2\right) \sin \mu - \mu \left(\mu^2 - 6\right) \cos \mu\right]}{\sin \mu - \mu \cos \mu} \tag{21}$$

When  $m_1$  represents the earth and  $m_2$  the moon, we find from this equation and the value of  $\mu$  given in (15) that

$$c_1 = c_2 = 0.33594 \tag{22}$$

instead of 0.4, the value for homogeneous spheres.

## V. SPECIAL CASE i=0 $i_1=0$ $a_2=0$ e=0 S=0.\*

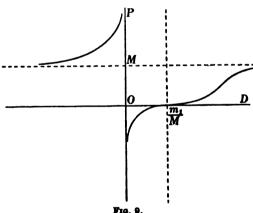
This means that two bodies undisturbed by any exterior force revolve in circles, that the radius, mass, and angular velocity of rotation of one of them are so small that its rotational momentum and energy may be neglected, and that the axis of rotation of the other is perpendicular to the plane of their orbit. In this case equations (9) and (10) become, writing D in place of  $D_1$ ,

$$M = P^{\frac{1}{2}} + \frac{m_1}{D} \tag{23}$$

$$\frac{E}{\pi} = -\frac{1}{P!} + \frac{m_1}{D^2} \tag{24}$$

We may choose the direction of revolution of the bodies as the positive direction. Then only a positive P can have a meaning in the problem, since a revolution in one direction can not be reversed without a collision of the bodies. D is positive or negative according as the rotation is in the same direction as the revolution or the opposite. Under the hypotheses adopted M is rigorously constant. When  $D = +\infty$  then  $P = M^2$ ; when  $D = \frac{m_1}{M}$  then P = 0; when  $D = \lim_{\epsilon \to 0} (0 + \epsilon)$  then  $P = -\infty$ ; when  $D = \lim_{\epsilon \to 0} (0 - \epsilon)$ 

 $D = \frac{m_1}{M}$  then P = 0; when  $D = \lim_{\epsilon \to 0} (0 + \epsilon)$  then  $P = -\infty$ ; when  $D = \lim_{\epsilon \to 0} (0 - \epsilon)$  then  $P = +\infty$ ; when  $D = -\infty$  then  $P = M^3$ . Consequently the curve defined by (23) is as given in fig. 9. The part of the figure to the right of the P-axis belongs to the case where the rotation of  $m_1$  and revolution of  $m_2$  are in the same direction, and the part to the left where they are in opposite directions.



The slope of the curve, or the ratio of the rate of change of the period of revolution to that of rotation, is found from (23) to be

$$\frac{dP}{dt} / \frac{dD}{dt} = \frac{3m_1P^{\frac{3}{4}}}{D^2}$$
 (25)

<sup>\*</sup> For a similar treatment of this problem see No. 5 of Darwin's papers.

The values of P and D must also satisfy equation (24). Starting from any epoch, P and D must change, if at all, so that E shall decrease, for if there is (tidal) friction in the system, some of its energy will degenerate into heat and be dissipated.

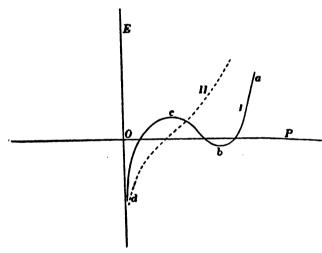
The relations between P and E and D and E are found from (23) and (24) to be respectively

$$P^{\frac{1}{2}} - 2MP^{\frac{1}{2}} - \frac{m_1}{P^{\frac{3}{2}}} = m_1 \frac{E}{\pi} - M^2$$
 (26)

$$\frac{m_1}{D^2} - \frac{D^2}{(MD - m_1)^2} = \frac{E}{\pi}$$
 (27)

In these equations P may vary only from 0 to  $+\infty$  while D may vary from  $-\infty$  to  $+\infty$ .

The curve whose equation is (26) has two forms according as E, considered as a function of P, has a finite maximum and minimum or not. In case there are a maximum and a minimum it has the form I, fig. 10. Since E can only decrease, it follows that if at  $t=t_0$  the period is on the part



F10. 10

of the curve ab it will decrease to the abscissa of the point b; if it is at b it will permanently remain at that value; if it is between b and c it will increase toward the value at b; if it is at c it will remain there unless the system suffers some exterior disturbance, when it will increase toward b or decrease toward d according to the nature of the disturbance; if it is between c and d it will continually decrease toward zero.

When the curve has no finite maximum and minimum it has the form II, and then whatever may be the value of P at  $t=t_0$  it will continually decrease toward zero with decreasing E.

It is unnecessary to draw the curve whose equation is (27), for the relation between the change in P and the change in D is given in (25).

It is seen from this equation that when the rotation and revolution are both in the same direction P and D either both increase or both decrease, if they change at all.

The necessary condition for a maximum or a minimum of E is, from (26),

$$\frac{3m_1}{2\pi}P^{\frac{1}{2}}\frac{\partial E}{\partial P} \equiv P^{\frac{1}{2}} - MP + m_1 = 0 \tag{28}$$

The corresponding condition from (27) is

$$\frac{D^3 (MD - m_1)^3}{2\pi m_1} \frac{\partial E}{\partial D} \equiv D^4 - M^2 D^3 + 3m_1 M^2 D^2 - 3m_1^2 MD + m_1^3 = 0$$

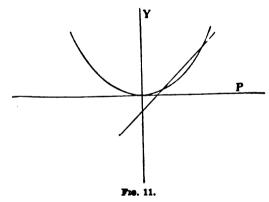
The only D having a physical meaning is real. Since no real negative D satisfies this equation, it follows that when D is negative E has no finite maximum or minimum. In this case by fig. 10, dotted curve, the period of revolution must always decrease and the two bodies ultimately fall together. Taking the last four terms to the right and extracting the cube root, we have,

$$D^{\bullet} = MD - m_1$$

Since the roots of this equation are the same as those of (28), it follows that when E is a maximum or minimum D = P and the system moves as a rigid body. The real roots of (28) are the abscissas of the intersections of the curves

$$y = P^{*} \qquad y = MP - m, \tag{29}$$

It is evident from fig. 11 that there are two, or no, intersections of these curves.



For a given  $m_1$  the value of M may always be taken so great that there will be two real roots; or, so small that there will be no real roots. The limiting value of M, as it decreases, for which the real roots exist is that value for which they are equal. The condition that (28) shall have equal roots is

$$\frac{4}{3}P^{1} - M = 0 (30)$$

Since this value of P must also satisfy (28) we have

$$\left(\frac{3}{4}\right)^4 M^4 - \left(\frac{3}{4}\right)^3 M^4 + m_1 = 0$$

$$M = \frac{4}{24} m_1^4 \tag{31}$$

whence

as the value of M for which there are two equal roots of (28). For greater values of M (28) has two distinct real roots. The roots are the abscissas of the points b and c, curve I, fig. 10. The smaller root corresponds to a maximum of E, and the larger to a minimum. When the roots are equal the curve has a point of inflection with tangent parallel to the P-axis.

the curve has a point of inflection with tangent parallel to the P-axis.

We may express the rates of change of P and D in terms of the rate of change of E by differentiating (23) and (24) and solving. We find

$$\frac{dP}{dt} = -\frac{3P^{1}D}{2\pi(P-D)}\frac{dE}{dt} \qquad \frac{dD}{dt} = -\frac{PD^{1}}{2m_{1}\pi(P-D)}\frac{dE}{dt} \qquad (32)$$

Consider the case first where the direction of rotation and revolution of  $m_1$  are the same, i.e., when D>0. Since  $\frac{dE}{dt}$  can be different from zero only when  $P \ge D$ , then when P > D both P and D must increase whatever may be the character of the tides as determined by the physical condition of  $m_1$ ; and when P < D both P and D must decrease. When  $m_1$  rotates in the negative direction, i.e., when D < 0, P must always decrease and D always numerically increase. When P = D equation (23) becomes

$$\frac{1}{P}(P^{1}-MP+m_{1})=0$$

for which, by (28), E is a maximum or minimum.

We are supposing the orbit a circle and the axis of  $m_1$  perpendicular to this orbit. Consequently when P=D there can be no change in the motion of the system due to the tides. Therefore the right members of (32) must carry  $(P-D)^j$  as a factor, where j > 1. The exponent j can not be fractional for then the rate of change of P would be imaginary for P < D. Consequently j is 2 or some greater positive integer. The velocity of the tide with respect to the surface of  $m_1$  is  $\frac{P-D}{PD}$ , and the tidal force is proportional to  $\frac{1}{r^3}$ . If we assume that the friction is proportional to the height of the tide and the first power of its velocity over the surface of  $m_1$ , and that the loss of energy, i.e., the work done against friction, is proportional to the square of the friction, equations (32) become

$$\frac{dP}{dt} = \frac{c_1}{r^6} \frac{P - D}{P^6 D} \qquad \frac{dD}{dt} = \frac{c_1}{m \cdot r^6} \frac{D(P - D)}{P}$$
(33)

where  $c_1$  is a constant depending upon the physical condition of  $m_1$ .

Equations (32) are very instructive, for they prove rigorously, under the hypotheses we have adopted in this section, that the rates of change of both the day and the month are proportional to the rate of the loss of energy, however it may be lost. That is, if tidal friction is now almost exclusively in the ocean tides, as Darwin supposed, in so far as the earthmoon system satisfies the hypotheses of this section it is quite immaterial whether the energy is lost in the manner described by the spherical harmonic analysis when applied to the viscous theory, or whether it degenerates after the waves have been time after time reflected from the continents and have run into narrow bays or into the high latitudes. relation of the tidal wave to the moon is not directly involved as it is in the elementary geometrical discussions of tidal friction, though of course the rate, and therefore the phase, of the friction depends upon the viscosity of the water. This would increase one's faith in the spherical harmonic analysis for such an earth and ocean as we have if it were not for the fact that the irregularities in the depth of the ocean and in the outlines of the continents undoubtedly greatly change the whole amount of friction.

The moon sets up motions in the waters of the ocean, but not all of the energy possessed by this water is lost. At the succeeding disturbance of the same region by the moon the phase of the tidal deformation still persisting may be such that the moon's attraction will tend to destroy it rather than generate a new wave; or, the phase may be such that the moon will augment the tide. On a world covered with oceans of many dimensions and depths we should expect to find places where the natural periods of oscillations in water basins are such that the moon's disturbance builds up considerable tides, and others where they are kept low. In the former case the friction of the water prevents their becoming excessively large; if the water were entirely frictionless they would increase until the resulting alteration in their period would lead to their destruction by the moon's disturbing forces.

One method of finding the present rate of tidal friction, at least so far as it is due to ocean tides, is to compute from tidal observations in all parts of the earth, and from the frictional properties of water, the actual waste of energy. If one were to observe the energy manifested when the tide runs through a strait on our coasts, he would be apt to overestimate the work the moon is doing upon the earth. In the first place such conditions are quite exceptional, and in the second place only a very small part of that energy degenerates into heat. When the run of the tide ceases the kinetic energy has very largely become potential, and it becomes kinetic again when the tide runs out. If the outgoing tide has the same energy as the inflowing tide there has, of course, been no loss, and, according to equations (32) and (33), there is no tidal evolution in such a system as we are considering in this section.

In the units employed the kinetic energy of rotation of  $m_1$ , the kinetic energy of revolution of  $m_1$  and  $m_2$  about their common center of mass,

 <sup>2,</sup> pp. 483-484.
 For a discussion of the observational evidence see Harris, U. S. Coast and Geod. Survey (1900), app. 7, pp. 535-699. Also Chamberlin's paper, ante, pp. 5-59.
 See paper by MacMillan, ante, pp. 71-75.

and the potential energy of  $m_1$  and  $m_2$  are respectively

$$E_{m_1}^{(\text{rotation})} = \frac{m_1 \pi}{D^2}$$
  $E_{m_1 + m_2}^{(\text{revolution})} = \frac{\pi}{P^{\frac{3}{2}}}$   $E_{m_1 + m_2}^{(\text{potential})} = \frac{-2\pi}{P^{\frac{3}{2}}}$  (34)

Then from equations (32), (33), and (34) we find

$$\frac{dE_{m_1}}{dt} = \frac{P}{P-D} \frac{dE}{dt} \quad \frac{dE_{m_1+m_2}}{dt} = \frac{D}{P-D} \frac{dE}{dt} \quad \frac{dE_{m_1+m_2}}{dt} = \frac{-2D}{P-D} \frac{dE}{dt} \quad (35)$$

whence

$$\frac{dE_{m_1}^{(\text{rot.})}}{dt} / \frac{dE_{(m_1+m_2)}^{(\text{rev.})}}{dt} = + \frac{P}{D} \qquad \frac{dE_{m_1}^{(\text{rot.})}}{dt} / \frac{dE_{m_1+m_2}^{(\text{pot.})}}{dt} = -\frac{P}{2D}$$
(36)

When the directions of the revolution and of the rotation are the same, the loss of energy of rotation is to that of revolution of both bodies as the period of revolution is to that of rotation, and the potential energy gains twice the loss of the revolutional energy.

The number of periods of rotation in one of revolution is, from (23),

$$N = \frac{P}{D} = \frac{P}{m_1} (M - P^{\frac{1}{2}})$$
 (37)

When (28) is satisfied N=1. The maximum value of N is defined by

$$m_1 \frac{\partial N}{\partial P} = (M - \frac{4}{3}P^{\frac{1}{3}}) = 0$$
 (38)

whence, at maximum N,

$$P = \frac{27}{64}M^2 \qquad N = \frac{27}{256}\frac{M^4}{m_1} \tag{39}$$

## VI. APPLICATION OF SECTION V TO THE EARTH-MOON SYSTEM.

This discussion neglects the rotational momentum and energy of the moon, the eccentricity of the moon's orbit, the inclination of the equator of the earth to the moon's orbit, the slight oblateness of the earth, and the disturbing action of the sun. These factors have probably been of slight importance in the series of changes which P and D may have undergone. The observations show that at present, taking for the radius of the earth that which would give it a volume equal to that of the actual oblate earth,

$$\begin{array}{lll} a_1 = 3,958.2 \text{ miles} & S = 332,000 \ m_1 \\ a_2 = 1,081.5 \text{ miles} & D = 0.997270 \text{ mean solar day} \\ r' = 92,897,000 \text{ miles} & P = 27.32166 \text{ mean solar days} \\ m_1 = 81.7 \ m_2 & P' = 365.25635 \text{ mean solar days} \\ \end{array} \right\}$$

From the two-body problem we have 1

$$k = \frac{2\pi r'^{\frac{1}{4}}}{P'\sqrt{S + m_1 + m_2}} \tag{41}$$

Consequently the second equation of (8) becomes

$$\frac{2\pi r'^2 m_1}{P'^{\frac{1}{2}} \left(\frac{m_1}{m_2} + 1\right)^{\frac{1}{2}} \left(\frac{S}{m_2} + \frac{m_1}{m_2} + 1\right)^{\frac{1}{2}}} = 1 \tag{42}$$

With the data of (40) the first equations of (8) and (42) give

unit of time = mean solar day 
$$a_1 = 0.688303$$
  
unit of length = 1.45285  $a_1$   $m_1 = 0.626311$   
unit of mass = 1.59665  $m_1$  (43)

Using (40) and (43), equations (23) and (24) become

$$M = 3.01187 + 0.62803 = 3.63990$$

$$E = -0.34632 + 1.95689 = 1.61057$$
(44)

It is found from (25) that at the present time the ratio of the rate of the change of the month to that of the day is

$$\frac{dP}{dt} / \frac{dD}{dt} = 17.14 \tag{45}$$

With the value of  $m_i$ , given above we find

$$\frac{4}{3!}m_1^{\frac{1}{4}}=1.56$$

 $<sup>^1</sup>$  There is, of course, a corresponding equation for the motion of the moon about the earth, but since the direct perturbing action of the sun increases the period for a given distance of the moon, the k found from this equation would be too small.

Since M is greater than this number it follows that (28) has two real roots. It is easily found by approximation processes that the roots of (28) are 1

$$P_1 = 0.20535 \text{ days} = 4.9284 \text{ hours}$$
  $P_2 = 47.705 \text{ days}$  (46)

Since the present value of P lies between these limits it must always remain between them and continually approach  $P_2$ . From the formula

$$P = \frac{2\pi a^{\frac{3}{4}}}{k\sqrt{m_1 + m_2}}$$

where k is the Gaussian constant, and the units are the mean solar day, r', and S, we find that the distances  $R_1$  and  $R_2$  corresponding to  $P_1$  and  $P_3$  are  $R_1 = 9,194.35 \text{ miles} \qquad R_2 = 345,355 \text{ miles} \qquad (47)$ 

The maximum possible number of days in a month is at once found from (39) to be N=29.559 (48)

The corresponding length of the month expressed in terms of present mean solar days is, from the first equation of (39),

$$P = 20.345 \tag{49}$$

Since the month is increasing and now greater than 20.3 days, the system is already beyond the condition of maximum number of days in a month.

Let us apply these results to Darwin's hypothesis of the separation of the moon from the earth by fission, remembering, of course, that a number of factors involved in the actual case have been omitted. At the time of separation their periods of rotation and of revolution about their center of gravity must have been equal. But the solution shows that they moved as a rigid body when the surface of the moon was 9,194.4-(3,958.2+1,081.5) = 4,154.7 miles from the surface of the earth, which contradicts the hypothesis that they had just separated by fission. But this is neglecting the earth's oblateness, which must have been great. To get an idea of the possibilities let us examine a number of modifying hypotheses. First let us suppose that the earth was then so oblate that its equator reached to the moon, and that the law of density was such as to keep its moment of momentum and volume unchanged. Then we find that

Obviously the spheroid would have broken up long before it attained this degree of oblateness, and under the hypothesis that the moment of momentum was as it would have been in a sphere the equatorial zone would have been so rare that one could not account for the matter in the moon.

In order to avoid the difficulty of the rare periphery, forced by the condition on the moment of momentum, we may waive this condition. Assuming simply that the earth was oblate, let us find the qualitative effects on the initial distance of the moon. The moment of momentum for

<sup>&</sup>lt;sup>1</sup> Darwin in 2, p. 508, taking the earth as a homogeneous spheroid and other data somewhat different, found  $P_1 = 5.6$  h.,  $P_2 = 55.5$  d.

a given volume will have been greater than that which we have used, and we may adjust our formulas for it by increasing the  $c_1$  which occurs in the original equations (6) and (7). It follows from (8) that the unit of length is now greater than before. Then by (42) the numerical value of  $m_1$  is greater than with the original  $c_1$ , from which it follows by (29) and fig. 11 that the distance of the moon from the earth when the month and day were equal was greater than that computed above. This would necessitate an increase in the oblateness in order that the earth's equator should have extended out to the moon, and the difficulty of having an earth already improbably oblate is increased.

Another hypothesis is that the earth was initially larger and, since the separation of the moon, has shrunk to its present dimension. This is quite in accord with the general ideas prevailing in the fission theory. We can not apply directly the formulas which have been written down because a change in volume would change the distance at which the system moved as a rigid body. Consider an instantaneous change of any extent in the radius of the earth. This does not change its rotational moment of momentum. Then if we employ the same units  $\frac{m_1}{D}$  is not changed; that is, D is changed so that when the new coefficient of  $m_1$  as defined in (8) and (42) is used the quotient is constant. But an increase in the size of the earth would result in an increase in D. Therefore  $m_1$  is increased to  $km_1$  and the condition for equality of the day and month is

$$P^{\mathbf{1}} - MP + km_1 = 0$$

From this equation we find

$$\frac{\partial P}{\partial k} = \frac{m_1}{M - 4P^1}$$

which is positive for the smaller root of  $P^{1}$ . Hence, if the earth has shrunk from larger dimensions, the earth and moon moved as a rigid system at a greater initial distance than that found above. That is, the hypothesis that the earth has shrunk only adds to the embarrassment because of the initial great distance of the moon.

We may try the hypothesis that the moon separated from the earth at a distance of 9,194.4 miles, that the earth's law of density was such that at that time its radius was equal to this number, and that the moment of momentum of the earth's rotation was the same as if its density were as it is at present. The latter condition is necessary, for the whole moment of momentum is unchanged by contraction. This hypothesis amounts to simply attempting to change the law of density as well as the volume so that the implications of the hypothesis shall be reasonably satisfied.

We shall suppose the density is expressible by the Laplacian law, only with different values of G and  $\mu$  from those which are used above. Letting  $R_1 = 9,194.4$ , the moment of momentum of the whole system was

$$M = 2\pi c' \left(m_1 + m_2\right) \frac{R_1^2}{P_1} = \frac{2\pi c' m_1}{P_1} \left(1 + \frac{m_2}{m_1}\right) \left(\frac{9,194.4}{20^{1/2}}\right)^2 a_1^2 \tag{50}$$

where c' depends upon the new law of density. We have in the units defined in (8)

$$c' = \frac{P_1 M}{m_1 \left(1 + \frac{m_2}{m_1}\right)} \left(\frac{3.958.2}{9.194.4}\right)^2 c_1 = 0.02017$$
 (51)

the  $c_1$ ,  $\frac{m_2}{m_1}$ ,  $m_1$ , M,  $P_1$ , and  $R_1$  being given in equations (22), (40), (43), (44), (46), and (47) respectively.

With this value of c' we must determine a new value of  $\mu$ , say  $\mu'$ , from (21). To facilitate the solution (21) may be written in the form

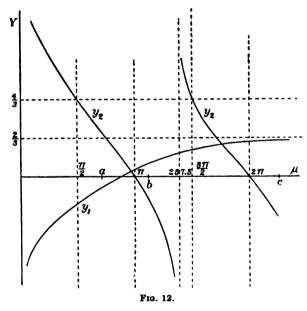
$$f(\mu') = \frac{2}{3} - c' - \frac{4}{\mu'^2} + \frac{4 \tan \mu'}{3 (\tan \mu' - \mu')} = 0$$
 (52)

We may draw the graph of this function. It is the sum of two functions

$$y_1 = \frac{2}{3} - c' - \frac{4}{\mu'^2} \tag{53}$$

and

$$y_2 = \frac{4 \tan \mu'}{3 (\tan \mu' - \mu')} \tag{54}$$



For  $\mu'=0$  we see that  $y_1=-\infty$  and  $y_2=+\infty$ , but that  $y_1+y_2=2-c'=1.98$ . The curve for  $y_1$  is very simple. The value of  $y_2$  is positive while  $\mu'$  varies from 0 to  $\pi$ , vanishing at  $\mu'=\pi$ . Then  $y_2$  becomes negative and remains negative until  $y_2=-\infty$  by the vanishing of tan  $\mu'-\mu'$  at  $\mu'=257^\circ$  30'. Then  $y_2$  changes sign and descends from  $+\infty$  to  $\frac{4}{3}$  at  $\mu'=\frac{3\pi}{2}$  and to zero

for  $\mu'=2\pi$ . Then it decreases to  $-\infty$  in the fifth quadrant, changes sign to  $+\infty$  and decreases to zero at  $\mu'=3\pi$  and to  $-\infty$  again in the seventh quadrant. In a general way this cycle of changes is repeated indefinitely, the points where  $y_2$  becomes infinite approaching nearer and nearer to  $\mu'=(2n+1)$   $\frac{\pi}{2}$ , n being an integer. The curves  $y_1$ ,  $y_2$  are given in fig. 12. Both  $y_1$  and  $y_2$  being even functions of  $\mu'$  the curves are entirely to the right of the vertical axis.

From the diagram it is seen that the only places where  $y_1 + y_2$  may vanish are at the left of  $\pi$  as at a, to the right of  $\pi$ , as at b, to the right of  $2\pi$ , as at c, and in general to the right of  $n\pi$ , n any integer. There are, in short, an infinite number of determinations of  $\mu'$ . But when we consider that the law of density is

$$\sigma' = \frac{G' \sin \mu' \frac{r_1}{R_1}}{\frac{r_1}{R_1}}$$

we see that if  $\pi < \mu' < 2\pi$  the density will be negative near the surface and elsewhere positive; if  $2\pi < \mu' < 3\pi$  there will be a single spherical layer between the center and surface where the density will be negative; and if  $n\pi < \mu' < (n+1)\pi$  there will be n layers of negative density if n is odd, one of them being at the surface, and n-1 layers of negative density if n is even, the surface density being positive. Consequently in considering such a practical question as the separation of the moon from the earth, in which negative densities would have no meaning, we need consider only the possibility of a solution to the left of  $\pi$ . The value of  $\mu'$ , for which  $y_1$  vanishes, is

$$\mu' = \frac{2\sqrt{3}}{\sqrt{2 - 3c'}} = 142.5^{\circ}$$

From fig. 12 it is seen that  $y_1 + y_2$  can not vanish between this point and  $\pi$ . It is easily verified that no value of  $\mu' < 142.5^{\circ}$  will satisfy (52). For example, we find the following corresponding sets of values

$$\begin{cases} \mu' = 0^{\circ} & 45^{\circ} & 90^{\circ} & 135^{\circ} & 140^{\circ} \\ f(\mu') = 0.58 & 0.40 & 0.38 & 0.33 & 0.32 \end{cases}$$

Consequently the smallest  $\mu'$  satisfying the conditions is greater than  $\pi$ , and the hypothesis of the separation of the moon from the earth requires, so far as the factors and the law of density here considered are concerned, that we assume that the surface density of the united mass was negative just previous to the separation. If we had used the oblateness of the figure of the mass, a still larger  $\mu'$  would have been found. However, it is not impossible that neglected factors may somewhat relieve the theory of these embarrassments.

Thus we see that when we add any of the hypotheses of an original oblateness, shrinking, or different law of density singly, the difficulties of the hypothesis are not relieved.

VII. CASE 
$$i=0$$
  $i_1=0$   $i_2=0$   $a_2 \neq 0$   $e=0$   $S=0.*$ 

This case differs from V only in that the rotational momentum and energy of  $m_2$  are not supposed to be zero. In this case equations (9) and (10) become, supposing that  $c_2 = c_1$ ,

$$M = P^{\frac{1}{2}} + \frac{m_1}{D_1} + \left(\frac{a_2}{a_1}\right)^2 \frac{m_2}{D_2}$$
 (55)

$$\frac{E}{\pi} = -\frac{1}{P^{\frac{3}{2}}} + \frac{m_1}{D_1^2} + \left(\frac{a_2}{a_1}\right)^2 \frac{m_2}{D_2^2}$$
 (56)

In these equations only P,  $D_1$ ,  $D_2$ , and E can vary, the last decreasing through loss of energy by friction. If by means of (55) we eliminate one of the variables from (56) we have a relation among the other three. This equation may be considered as defining a surface. Let the E-axis be pointed upward. Then starting from any point on the surface the variables other than E may change in any way, so far as these considerations show, so that the point descends.

We shall now find the maximum and minimum values of E. In order to simplify the algebra let us put

$$u = \frac{m_1}{D_1} \qquad v = \left(\frac{a_2}{a_1}\right)^2 \frac{m_2}{D_2} = \frac{\kappa m_1}{D_2}$$
 (57)

Using this substitution and eliminating P between (55) and (56) we obtain

$$\frac{E}{\pi} = \frac{-1}{[M - u - v]^2} + \frac{u^2}{m_1} + \frac{v^2}{\kappa m_1}$$
 (58)

The necessary conditions for a maximum or minimum of E are

$$\frac{m_{1}[M-u-v]^{3}}{2\pi} \frac{\partial E}{\partial u} \equiv -m_{1}+u [M-u-v]^{3} = 0$$

$$\frac{\kappa m_{1}[M-u-v]^{3}}{2\pi} \frac{\partial E}{\partial v} \equiv -\kappa m_{1}+v[M-u-v]^{3} = 0$$
(59)

Multiplying the first equation by v, the second by u, and taking their difference, we have  $\kappa u = v$ ; whence, by (57),

$$D_2 = D_1 \tag{60}$$

Then the first equation of (59) becomes

$$-\frac{m_1}{u} + [M - (1+\kappa)u]^3 = 0 (61)$$

<sup>\*</sup> See 5, pp. 178-181.

which, after extracting the cube root, is

$$M = \left(\frac{m_1}{u}\right)^{\frac{1}{2}} + (1+\kappa)u$$

Let the common value of  $D_1$  and  $D_2$  be D. Then this equation becomes

$$M = D^{\frac{1}{2}} + (1 + \kappa) \frac{m_1}{D} = D^{\frac{1}{2}} + \left[m_1 + \left(\frac{a_2}{a_1}\right)^2 m_2\right] \frac{1}{D}$$
 (62)

But when  $D_1 = D_2 = D$ , (55) becomes

$$M = P^{\frac{1}{2}} + \left[m_1 + \left(\frac{a_2}{a_1}\right)^2 m_2\right] \frac{1}{D}$$
 (63)

where  $P^{\dagger}$  must be taken with the positive sign. Since (62) and (63) must simultaneously be satisfied for a maximum or minimum, we must have, when E is a maximum or minimum,

$$P = D_1 = D_2 \tag{64}$$

That is, the energy is at a maximum or minimum only if  $P = +D_1 = +D_2$ , i.e., if the whole system moves as a rigid body.

There can be a maximum or minimum only if (62) has real roots. The treatment of this question is the same as that given in IV, except that we must replace  $m_1$  of that section by  $m_1 + \left(\frac{a_2}{a_1}\right)^2 m_2$ . Hence the condition for real roots, and therefore for a maximum and a minimum of E, is, by (31),

$$M \ge \frac{4}{3^{\frac{1}{4}}} \left[ m_1 + \left( \frac{a_2}{a_1} \right)^2 m_2 \right]^{\frac{1}{4}} = \frac{4}{3^{\frac{1}{4}}} (1 + \kappa)^{\frac{1}{4}} m_1^{\frac{1}{4}}$$
 (65)

Let us suppose the inequality (65) is satisfied and then consider the surface defined by (58). It will be most convenient to give E a series of constant values and to draw the corresponding equi-energy curves. To simplify the treatment let

$$w = u + v \tag{66}$$

Eliminating u from (58) by means of this equation and solving for v we find

$$\frac{\kappa + 1}{\kappa} v = w \pm \sqrt{-\frac{w^2}{\kappa} + \frac{(1 + \kappa)m_1}{\kappa(M - w)^2} + \frac{(1 + \kappa)m_1E}{\kappa\pi}}$$
 (67)

Consider first the function

$$f(w) = -\frac{w^2}{\kappa} + \frac{(1+\kappa)m_1}{\kappa(M-w)^2} + \frac{(1+\kappa)m_1E}{\kappa\pi}$$
 (68)

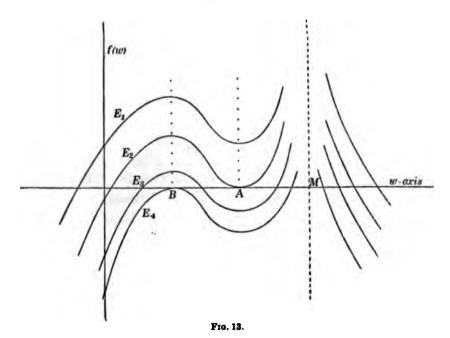
whence

$$\frac{\kappa+1}{\kappa}v = w \pm \sqrt{f(w)} \tag{69}$$

The derivative of (68) is

$$\frac{\partial f(w)}{\partial w} = -\frac{2w}{\kappa} + \frac{2(\kappa + 1)m_1}{\kappa (M - w)^2} \tag{70}$$

It depends only upon w and is negative for all w > M. For w = M it is infinite. For w less than, but near to, M it is positive; when M is large it vanishes and becomes negative and again vanishes and becomes positive, as w decreases from M to 0. It is positive for all w < 0. From these facts and equation (68) fig. 13 is drawn, the curves  $E_1$ , . . .,  $E_4$  belonging to four values of E such that  $E_1 > E_2 > E_3 > E_4$ .



From equation (69) and fig. 13 the equi-energy curves in fig. 14 are drawn, the corresponding curves being similarly lettered. There are two points of particular interest, A and B. As the energy decreases, the energy curves descend to a point at A. That is, on a section through A approximately parallel to the vE-plane the point A is a minimum. With decreasing E the energy curves separate at A and recede in opposite directions nearly parallel to the w-axis. Hence a section by a plane through A approximately parallel to the wE-plane has the point A as a maximum. Therefore A is a minimax point of the surface.

The minimax point A, fig. 14, corresponds to the point A, fig. 13, at which f(w) = 0. Therefore, by (69), for this point

$$v = \frac{\kappa}{\kappa + 1} w \tag{71}$$

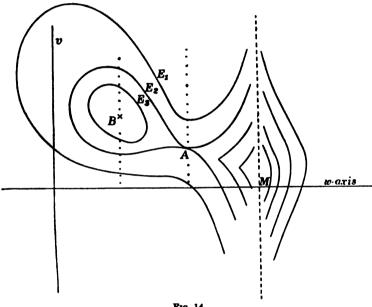
At the point A, fig. 13, we have also

$$\frac{\kappa}{2}\frac{\partial f(w)}{\partial w} = -w + \frac{(\kappa+1)m_1}{(M-w)^2} = 0$$

which becomes by virtue of (71) and (66)

$$-\frac{m_1}{u} + [M - (\kappa + 1)u]^2 = 0$$

agreeing with (61), the condition for a maximum or minimum (or minimax).



F16. 14.

The point B of fig. 14 corresponds to the point B of fig. 13. At the point B, fig. 13, we have

$$f(w) = 0 \qquad \frac{\partial f(w)}{\partial w} = 0$$

which lead again to equation (61). Therefore the smaller real root of (61) belongs to a minimum and the larger to a minimax.

However the system may change under loss of energy the w and v of fig. 14 must always go from a curve of higher to one of lower energy. When the energy is greater than that for which the point A appears in fig. 14, the curves give us no positive knowledge regarding the series of changes the system may undergo, except that if at any time w=u+v < M it has always been, and will always be, less than M, and the opposite. But if the energy is less than that for which A appears in fig. 14, then, if at any time the w belonging to the system is less than the abscissa of A, that is, if the point is on the curve  $E_s$ , it will always remain less than the abscissa of A and will approach the point B as a limit; but if the w is greater than the abscissa of A and less than M it will always remain between these two values. The abscissa of every point on the oval part of  $E_s$  is in all possible cases less than the abscissa of A, for the points on this branch of the curve correspond to the points of the curve  $E_s$  of fig. 13 which are above the w-axis and to the left of the line w=M. This part of the curve is always to the left of A, for the curves of fig. 13 are all derivable from any one of them simply by vertical displacements.

A simple case is that in which the two bodies are precisely alike in every respect and have at any time similar motions. Then from the symmetry of the problem the motions of the two bodies will always be the same. Equations (55) and (56) become in this case

$$M = P^{\frac{1}{2}} + \frac{2m_1}{D} \qquad \frac{E}{\pi} = -\frac{1}{P^{\frac{3}{2}}} + \frac{2m_1}{D^2}$$
 (72)

The treatment of these equations is precisely like that of (23) and (24) of section V if we replace  $m_1$  of that section by  $2m_1$ .

## VIII. APPLICATION OF SECTION VII TO THE EARTH-MOON SYSTEM.

With the data given in (40) we find

$$\left(\frac{a_2}{a_1}\right)^2 m_2 = \kappa m_1 = 0.000914 m_1 \tag{73}$$

Consequently the moment of momentum and energy of the earth-moon system are respectively

$$M = 3.01187 + 0.62803 + 0.00002 = 3.63992$$

$$E = -0.34632 + 1.95689 + 0.00001 = 1.61058$$
(74)

The limiting value of M for which a maximum or minimum may occur is, by (65), 1.5614. Since the actual M is greater than this quantity there are a minimax and a minimum.

We shall now solve (61) and find the value of u corresponding to the minimax. With the values of  $\kappa$  and M given in (73) and (74) we find by methods of approximation that the value of u satisfying (61) and corresponding to the minimax is

$$u = 3.04719 \qquad w = 2u = 6.09438 \tag{75}$$

The corresponding common period of the system and distance of the moon are respectively

$$P_1 = 0.20554 \text{ day} = 4.9329 \text{ hours}$$
  $R_1 = 9,200 \text{ miles}$  (76)

or more than 42 miles greater than when the moon's rotational momentum and energy were neglected. The whole energy of the system for this value of u = v is E = 10.666(77)

At the present time in the earth-moon system we find from the data of (40) and (73) and the condition  $D_2 = P$  that

$$u = 0.6280257$$
  $v = 0.0000005$   $w = u + v = 0.6280262$  (78)

Since the present energy, given in the second equation of (74), is less than that corresponding to A of fig. 13, which is given in (77), and since the present value of w given in (78) is less than that corresponding to A, given in (75), the energy will continually approach the value corresponding to the minimum B, when the earth-moon system will move as a rigid body. Although it is thus possible, under the hypotheses, to draw positive conclusions as to the conditions toward which the system is tending, it is, of course, not possible to affirm, even aside from all factors neglected in this section, that the system ever descended from the condition corresponding This discussion simply gives the numerical values belonging to the condition corresponding to A, which may or may not have been verified. Thus the real question of interest gets no conclusive answer by supposing the moon of finite size; the introduction of this factor simply embarrasses the fission theory a little more.

#### IX. APPLICATION TO BINARY STAR SYSTEMS.

If the earth and moon were derived by the fission of a parent mass, the process has presumably been exemplified elsewhere. We shall conclude that the earth has had an exceptional origin only as a last resort. It has been many times suggested that the binary stars may have originated by the breaking up of larger masses, and See especially has urged this view and applied Darwin's formulas in an attempt to explain the dimensions and eccentricities of their orbits.<sup>1</sup>

We shall apply the methods developed here to the problem. In order to simplify it as much as possible we shall suppose first that the parent mass divided into two similar and equal masses. We know that this relation of the masses of the two members of binary stars is, in a number of cases, nearly fulfilled, and nothing is known to make this assumption seem improbable. We shall assume that immediately after the fission the system moved as a rigid mass. Then the equations for the moment of momentum and energy are

 $M = P^{\frac{1}{2}} + \frac{2m_1}{D} \qquad \frac{E}{\pi} = -\frac{1}{P^{\frac{3}{2}}} + \frac{2m_1}{D^2}$  (79)

differing from those in section V only in that  $m_i$  has been replaced by  $2m_i$ . The condition for a maximum or minimum of E is [cf. eq. (28)]

$$P^{1} - MP + 2m_{1} = 0 (80)$$

As has been shown, when M is sufficiently large this equation has two real roots. The smallest M for which there are real roots is that for which the real roots are equal. The condition for equal roots of (80) is

$$M = \frac{4}{3}P^{\frac{1}{3}} = \frac{4}{3}\sqrt[4]{6m_1} \tag{81}$$

Consider the system moving as a rigid body with the two stars in contact. Then their orbital moment of momentum will be  $\frac{1}{c_1}$  times their rotational moment of momentum, or

$$P^{\frac{1}{2}} = \frac{2m_1}{c_1 D}$$
, (and  $P = D$ ) (82)

Consequently the whole moment of momentum of the system is, calling this special value of the common period  $P_0$ ,

$$M = (1 + c_1) P_0^{\frac{1}{2}} \tag{83}$$

In order that this may be at least as great as the value defined in (81) we must have

$$c_1 = \frac{1}{3} \tag{84}$$

The value of  $c_1$  depends only upon the law of variation of density of the bodies. When they are homogeneous  $c_1 = 0.4$ . When the density varies

<sup>&</sup>lt;sup>1</sup> Inaugural Dissertation, Berlin, 1892.

according to the Laplacian law and vanishes at the surface ( $\mu=180^{\circ}$ ), we find from (21) that  $c_1=0.26$ . The more the matter is condensed toward the centers of the bodies, the smaller in general  $c_1$  will be. It is apparent from these figures that  $c_1$  can not be much greater than 0.33, and therefore that M can not greatly exceed the value for which there are equal roots. Consequently the two roots of (80) can differ but little, which means that tidal friction is not competent to drive two equal stars originating in this way far from each other.

Let us suppose  $c_1 > 0.33$  so that E has both a maximum and a minimum. By (82) we have  $2m_1 = c_1 P_0^{\frac{1}{2}}$ . Using the value of M given in (83), equation (80) becomes

$$P^{\frac{1}{2}} - (1 + c_1)P_{0}^{\frac{1}{2}}P + c_1P_{0}^{\frac{1}{2}} = 0$$
 (85)

Since one of the roots of this equation is  $P_0^{\frac{1}{2}}$  we may factor it into  $P^{\frac{1}{2}} - P_0^{\frac{1}{2}}$  and

$$P - c_1 P_0^{\dagger} P^{\dagger} - c_1 P_0^{\dagger} P^{\dagger} - c_1 P_0 = 0$$
 (86)

whose real root gives the minimum value of E. To solve this cubic in  $P^{1}$  let

$$H = -\frac{1}{3} \left( 1 + \frac{c_1}{3} \right) c_1 P_0^{\frac{3}{2}} \qquad G = -\left( 1 + \frac{c_1}{3} + \frac{2c_1^2}{27} \right) c_1 P_0$$

$$p = \frac{1}{2} \left( -G + \sqrt{G^2 + 4H^3} \right) = \frac{1}{2} \left[ 1 + \frac{c_1}{3} + \frac{2}{27} c_1^2 + \sqrt{1 + \frac{14}{27} c_1 + \frac{1}{9} c_1^2 - \frac{8}{729} c_1^4} \right] c_1 P_0$$
(87)

Then by the theory of cubic equations 1

$$P_{1} = \frac{c_{1}}{3} P_{0}^{\frac{1}{3}} + \sqrt[3]{p} - \frac{H}{\sqrt[3]{p}} = F(c_{1}) P_{0}^{\frac{1}{3}}$$
(88)

Let us apply these equations to the case of two stars each equal in mass and dimensions to the sun. Taking the radius of the sun at 433,000 miles, we find from

$$P_0 = \frac{2\pi a^{\frac{1}{2}}}{k\sqrt{m_1 + m_2}}$$

that in this case

$$P_0 = 0.2324$$

We shall take for  $c_1$  the largest possible value, that is 0.4, which belongs to a homogeneous sphere. We find from (88) the corresponding largest value of  $P_1$  to be

$$P_1 = 0.307$$

which is the period for a separation of the centers of the bodies of 1,042,400 miles. The original separation was 866,000 miles. That is, under the assumption that each of the two components of a binary system is equal to the sun in mass and volume, and that they remain of constant size and

<sup>&</sup>lt;sup>1</sup> Burnside and Panton, Theory of Equations, p. 108.

shape, we have proved rigorously that after fission, tidal friction can not have increased their initial distance more than 200,000 miles. Such an inconsiderable increase as this in the distance between two stars can have had no important effects on binary systems. If the system started at the configuration corresponding to maximum energy of the curve of fig. 10, either it must have gone toward the condition of minimum energy just computed, or the two bodies must have fallen together.

Let us suppose the bodies to have shrunk as a consequence of loss of heat so that their period of rotation would have become, except for tidal friction,  $\kappa D$ . Since the rotational moment of momentum is not changed by shrinking, the  $m_1$  becomes  $\kappa m_1$ , the mass changing its numerical value because the definition of units depends upon the dimensions of the bodies. Then equations (79) become

$$M = P^{\frac{1}{2}} + \frac{2\kappa m_1}{\kappa D} \qquad \frac{E}{\pi} = -\frac{1}{P^{\frac{3}{2}}} + \frac{2\kappa m_1}{\kappa^2 D^2}$$
 (89)

Eliminating D we have

$$\frac{E}{\pi} = -\frac{1}{P^{\frac{3}{2}}} + \frac{(M - P^{\frac{1}{2}})^2}{2\kappa m_1} \tag{90}$$

The condition for a maximum or a minimum of E is

$$P! - MP + 2\kappa m_1 = 0 (91)$$

From the derivative  $\frac{\partial P}{\partial \kappa} = \frac{-2m_1}{\frac{1}{2}P^{\frac{1}{2}}-M}$  it follows that, for given values of M and  $m_1$ , the smaller  $\kappa$  is the farther apart are the two roots of P. Let the common initial value of P and D be  $P_0$ . Then equation (91) becomes, by (82) and (83),

$$P^{i} - (1 + c_{i})P_{0}^{i}P + \kappa c_{i}P_{0}^{i} = 0$$
(92)

Since this equation is homogeneous in P and  $P_0$ , its solution is of the form

$$P^{\frac{1}{2}} = f(c_1, \kappa) P_0^{\frac{1}{2}} \tag{93}$$

For a given amount of shrinkage of a body the constant  $\kappa$  is determined, because the moment of momentum is not changed by a decrease or increase of volume. Hence, if we assume an initial  $P_0$  and the  $\kappa$ , we may determine the final (and greatest) P from (92), and compare the results with the data given by observations of double stars. Or more simply, we may assume a final P in accord with the data furnished by observations and compute the  $\kappa$  from

$$\kappa = \frac{P[(1+c_1)P_0^{\frac{1}{6}} - P^{\frac{1}{6}}]}{c_1P_0^{\frac{1}{6}}}$$
 (94)

for various assumed values of  $P_0$ . Since the two stars are supposed to have been initially in contact, the initial density may be expressed in terms of  $P_0$ , and the final density is determined by the initial density and the amount

of shrinking, which is measured by  $\kappa$ . Therefore the final density may be determined, by the use of (94), in terms of the initial density and the final period.

We shall assume that P=100 years, or approximately the period of a Centauri and  $\xi$  Scorpii. There are many binaries known with much longer periods than this, as well as many with shorter periods. Since they have presumably all originated in a similar manner, any correct theory must explain the long periods as well as the shorter ones. We shall assume that the bodies have always remained homogeneous, whence  $c_1=0.4$ , which has been shown to be most favorable to the theory of a large increase of period through tidal friction. From the formula for the period in the two-body problem we find, using the volume times the density for the masses, and assuming that the bodies were originally in contact, that  $P_{\bullet}$  varies inversely as the square root of  $\sigma_{\bullet}$ , or

$$P_{\bullet} = \frac{\text{constant}}{\sqrt{\sigma_{\bullet}}} \tag{95}$$

The constant of this equation is determined by the fact that the density of the sun is 1.41, while in the case of two such stars as the sun we have found  $P_{\bullet}$  to be equal to 0.2324. Therefore the constant is 0.2760.

From the fact that the moment of momentum of a body simply shrinking must remain constant, we find that

$$a_1 = a_1{}^{(0)}\sqrt{\kappa} \tag{96}$$

where  $a_i^{(0)}$  is the initial radius and  $a_i$  the final. Since the density varies inversely as the cube of the radius we have

$$\sigma_1 = \left[\frac{a_1^{(0)}}{a_1}\right]^3 \sigma_0 = \frac{\sigma_0}{\kappa^3} = \text{final density}$$
 (97)

By formulas (94), (95), and (97), with P=100 years,  $c_1=0.4$ , the following table has been computed:

<b>6</b> 0	$P_0$	ĸ	σι
1.4	0.2324 day	20,650,000	$\frac{\sqrt{-1}}{18\times10^6}$
1010	36.4 years	0	<b>∞</b>
3.8 1010	38.8 "	0.19	45 1010
3.6 1010	39.9 "	0.25	$\frac{28.6}{10^{10}}$
3.0 1010	43.7 "	0.46	9.7 10 <sup>10</sup>
1010	72.8 "	1.03	3.8 1010

With an initial density of 1.4 the final density comes out imaginary, indicating that incompatible conditions have been imposed. That is, it is impossible for a star having the density and twice the mass of the sun to divide and be driven by tides into a binary system having a period of 100 years. When  $\sigma_0 = 4 \times 10^{-10}$  the final density is infinite, another impossible result. When the initial density is  $10^{-10}$  we find  $\kappa = 1.03$ , indicating an expansion instead of a contraction. The only initial densities compatible with the assumptions lie between  $4 \times 10^{-10}$  and  $10^{-10}$ . Consequently a double star having two equal components with combined mass twice that of our sun and a period of 100 years could not originate by fission except when it was in the nebulous state with a mean density not exceeding  $\frac{3}{10^6}$  of that of our atmosphere at sea-level. On the other hand, if the close binaries revealed by the spectroscope have originated by the fission of a single star, their period can never become great through the effects of their mutual tides. It follows from (92) that this relation between the initial period and final period depends only upon the law of density and the amount of the contraction, and is entirely independent of the mass of the system.

The question may be raised whether the results would not be less unfavorable to the theory if the mass of the system were unequally divided between the two stars. The discussion of section VII shows that the problem remains in a general way the same,  $2m_1$  being replaced simply by  $m_1 + \left(\frac{a_2}{a_1}\right)^2 m_2$ .

We must conclude from this discussion that approximately equal binary stars with long periods can have originated by the fission process only when the parent mass was yet in the nebulous state. In fact, it removes the chief support of the belief that there is any such thing as fission among the stars simply because of rapid rotations. From other considerations Jeans 1 has arrived at the same conclusion.

<sup>&</sup>lt;sup>1</sup>The Astrophysical Journal, XXII (1905), p. 101.

CASE X. 111

**X.** CASE 
$$i=0$$
  $i_1=0$   $i_2=0$   $a_3=0$   $e \neq 0$   $S=0.*$ 

In this case equations (9) and (10) become

$$M = P^{\frac{1}{6}} \sqrt{1 - e^2} + \frac{m_1}{D} \qquad \frac{E}{\pi} = -\frac{1}{P^{\frac{3}{6}}} + \frac{m_1}{D^2}$$
 (98)

Eliminating D and P in turn between these equations, we get

$$\frac{m_1 E}{\pi} = -\frac{m_1}{P^{\frac{1}{2}}} + \left[M - P^{\frac{1}{2}}\sqrt{1 - e^2}\right]^2 \qquad \frac{E}{\pi} = -\frac{(1 - e^2)D^2}{(MD - m_1)^2} + \frac{m_1}{D^2} \quad (99)$$

Solving for e we obtain

$$e = \frac{\sqrt{P^{\frac{1}{2}} - \left[M \pm \sqrt{\frac{m_1 E}{\pi} + \frac{m_1}{P^{\frac{1}{2}}}}\right]^2}}{P^{\frac{1}{2}}} \quad e = \sqrt{1 - \left(\frac{m_1}{D^2} - \frac{E}{\pi}\right) \frac{(MD - m_1)^2}{D^2}} \quad (100)$$

The conditions for a maximum or a minimum of the first of (99) are

$$\frac{m_1}{2\pi} \frac{\partial E}{\partial e} = P^{\frac{1}{2}} \left[ \frac{M}{\sqrt{1 - e^2}} - P^{\frac{1}{2}} \right] e = 0$$

$$\frac{3m_1}{2\pi} P^{\frac{1}{2}} \frac{\partial E}{\partial P} = P^{\frac{1}{2}} (1 - e^2) - \sqrt{1 - e^2} MP + m_1 = 0$$
(101)

The first equation may be satisfied by the vanishing of any of its three factors.  $P^{i}=0$  is a physical impossibility and makes E infinite. Setting the second factor equal to zero and substituting in the second equation we have  $m_{i}=0$ , which is impossible. The remaining possibility is  $\epsilon=0$ , and then equations (101) reduce to

$$e = 0$$
  $P^{1} - MP + m_{1} = 0$  (102)

the second equation being precisely the same as (28).

Similarly the second equation of (99) gives as the conditions for a maximum or a minimum

$$e=0$$
  $-D^{4}(MD-m_{1})+MD^{5}-m_{1}(MD-m_{1})^{3}=0$  (103)

The latter of these equations gives

$$D^{\frac{1}{2}} - MD + m_1 = 0 (104)$$

which, together with the second of (102), shows that for either a maximum or a minimum

<sup>\*</sup> See 3, parts V and VI, and the appendix, pp. 886-891.

We shall now study the surface defined by the second equation of (100) by considering the curves for various values of E. Consider first the curves defined by

$$y_1 = 1 - \frac{m_1}{D^2} \left( M - \frac{m_1}{D} \right)^2 \tag{105}$$

$$y_2 = \frac{E}{\pi} \left( M - \frac{m_1}{D} \right)^2 \tag{106}$$

From

$$\frac{\partial y_1}{\partial D} = \frac{2m_1}{D^2} \left( M - \frac{m_1}{D} \right) \left( M - \frac{2m_1}{D} \right) \tag{107}$$

we find the positions of the maxima and minima of  $y_1$  and we can then easily construct its graph.

We must now consider the curves defined by equation (106) for various values of E, both positive and negative. They all pass through the point  $y_2=0$ ,  $D=\frac{m_1}{M}$ , and are tangent to the D-axis at this point. All the branches of the curves are asymptotic to the lines D=0 and  $y_2=EM^2/\pi$ , except in the special case when E=0.

The sum  $y=y_1+y_2$  must then be considered. Whatever the value of E, all of these curves are asymptotic to D=0 and  $y=-\infty$ . All of the curves pass through the point  $D=\frac{m_1}{M}$ , y=1, and their slope is zero at this point. Their slope vanishes at the points defined by

$$\frac{\partial y}{\partial D} = \frac{2m_1}{D^2} \left[ M - \frac{m_1}{D} \right] \left[ \frac{E}{\pi} + \frac{M}{D} - \frac{2m_1}{D^2} \right] = 0$$
 (108)

The solutions of this equation are  $D=\pm\infty$ ,  $D=\frac{m_1}{M}$ , and the two roots of the last factor. When E is large the roots are small numerically, one being positive and the other negative. With decreasing E the negative root recedes to  $-\infty$  which it attains at E=0. It then becomes positive from  $+\infty$  and unites with the other positive root when

$$E = -\frac{M^2\pi}{8m_1}$$

The curve has a point of inflection for this value of E, for which  $D = \frac{4m_1}{M}$ , and for smaller values of E the slope is always negative for values of D greater than  $\frac{m_1}{M}$ .

Those curves which are tangent to the axis are found by imposing the condition (108) and

$$y_1 + y_2 = e^2 = 0 (109)$$

The first factors of (108) give no results of interest. Eliminating E between the third factor and equation (109) we get

$$D - \left(M - \frac{m_1}{D}\right)^2 = 0$$

agreeing with (103), the conditions for a maximum or a minimum. If equation (103) has no real roots then there is but one intersection of each curve with the D-axis to the right of  $D = \frac{m_1}{M}$ . When the equation has real roots then for certain values of E there are three intersections to the right of  $D = \frac{m_1}{M}$ . As E approaches  $-\infty$  the curves approach the line  $D = \frac{m_1}{M}$  between y = 0 and y = +1.

We get the final equi-energy curves from

$$e = \pm \sqrt{y} = \pm \sqrt{y_1 + y_3}$$
(110)
$$P_{10}, 15.$$

They are given in fig. 15. The point A is one of the solutions of (103) and is a minimax of E considered as a function of D and e. When this point belongs to a positive value of E, as it does in the earth-moon system, the curves for this and larger values of E are open on the right to infinity, because the curves are asymptotic to the lines  $e = \pm \sqrt{1 + \frac{EM^2}{\pi}}$ . When E decreases until  $EM^2 = -\pi$  the curves close at  $+\infty$ , and for smaller values of E they are closed ovals until they vanish at a point E on the E-axis to the right of E. This point corresponds to a true minimum of E considered as a function of E and E. On the left of the E-axis the curves are shaped

somewhat like parabolas and vanish at  $-\infty$  for  $EM^2 = -\pi$ . They are the

analytic continuations of the curves on the right, the union being at infinity. When K recedes to  $-\infty$  as  $E = \frac{M^2}{\pi}$  it reappears at  $+\infty$  as E continues to decrease to decrease.

It follows from (105) and (106) that  $y_1 + y_2 < 1$  for all negative values of E. Consequently for all points on the closed ovals we have |e| < 1, and the system can not be wrecked by a collision of the bodies. Therefore, if at any time the configuration of the system corresponds to any point on one of the closed ovals to the right of A, it will always tend with decreasing E through tidal friction toward the configuration corresponding to the point B, and the evolution will end with this configuration. Because of the symmetry of fig. 15 with respect to the line e=0, it follows that if at any time e=0 it will always remain zero.

While under certain conditions the system will inevitably progress toward a definite configuration, in the general case it is not possible, without hypotheses as to the physical condition of the bodies, to determine the character of the evolution. The question of greatest interest in the present connection arises in the case where the conditions lead to doubtful results.

If the moon separated from the earth by fission and if its orbit were originally circular, it would not become elliptic through tidal friction. Since the orbit is now considerably eccentric, we must assume that it was somewhat eccentric at the time of separation. Consequently, let us suppose the moon has just separated from the earth so that P = D, and, supposing that e=0, let us find whether the moon will fall again to the earth or recede from it. Since the orbital velocity will have been such that the moon's motion will have fulfilled the law of areas, while the rotational velocity will have been uniform, there will have been relative motion of the various parts of the system, and consequently tidal friction. We are to find the effects of this loss of energy on the distance of the moon.

Under what seem reasonable assumptions we have seen in section V, equations (33), that when the orbits are circular the rate of change of the month is given by

$$\frac{dP}{dt} = \frac{c}{r^6} \frac{P - D}{P^{\frac{1}{2}}D}$$

We shall now assume that when the orbit is elliptic the rate of loss of energy at any instant depends upon the square of the product of the tideraising force and the angular velocity of the tide over the earth. assumption is equivalent to taking the circular case as applying instantaneously to the elliptic case, and omits the lag in tidal conditions due to inertia. With this assumption the equation above becomes

$$\frac{dP}{dt} = -\frac{c'}{r^6} \frac{\theta - \omega^*}{\theta!} \tag{111}$$

where c' is a positive constant.

<sup>\*</sup>This result agrees with that found by Darwin in 2, p. 497, eq. (79) after change of variables, notation, and proper specialization of his problem.

CASE X. 115

By hypothesis the mean value of  $\theta$  is equal to  $\omega$ , and we have therefore from the two-body problem

$$\theta = \omega \left[ 1 + 2e \cos \omega t + \frac{5}{2} e^2 \cos 2\omega t + \dots \right]$$

$$r = a \left[ 1 - e \cos \omega t + \frac{e^2}{2} (1 - \cos 2\omega t) + \dots \right]$$
quation (111) becomes

Consequently equation (111) becomes

$$\frac{dP}{dt} = -c''e \left[ 2\cos\omega t + \frac{14}{3}e + \frac{43}{6}e\cos 2\omega t + \dots \right]$$
 (113)

where c" is a positive constant. The first and third terms produce no secular results. The second shows that P secularly decreases. That is, under the hypothesis that the loss of energy is proportional to the square of the product of the velocity of the tidal wave and the magnitude of the tide-raising force, it follows that if the moon had separated from the earth and originally had been moving around it in a slightly eccentric orbit in a period equal to that of the rotation of the earth, then the friction of the tides generated by the moon in the earth would have brought the moon back to the earth. Since these hypotheses certainly approximate the truth, we are led to the very probable conclusion that the moon can not have separated from the earth in an elliptic orbit and have been driven out to its present position by tidal friction.

Precisely similar reasoning applies to the hypothesis of the fission of a star into a pair of equal stars, and is an additional strong argument against the soundness of this theory regarding the origin of binary stars, which generally have large eccentricities.

<sup>&</sup>lt;sup>1</sup> Under the assumption that the planet is viscous and with different approximations, Darwin's equations led to the same result. See 3, p. 854, eq. (292), also 3, p. 878 and p. 891

#### XI. APPLICATION OF CASE X TO THE EARTH-MOON SYSTEM.

Observations show that in the case of the moon's orbit  $\epsilon = 0.0549$ . Then we find from (98) that in this case

M = 3.63082 E = 1.61057

Consequently for the moon at present the curves of fig. 15 are yet open at infinity, and so far as this discussion goes, the eccentricity may increase to unity, and the system be wrecked by a collision of the earth and moon.

The most interesting question relates to the least possible distance of the earth and moon from each other. Suppose at the time of the assumed separation the eccentricity of the orbit was very small, as apparently it must have been if the bodies separated by fission. Then the configuration at the time of separation corresponds to the point A of fig. 15. The abscissa of this point is the smaller real root of equation (104), which for the present value of M we find to be

#### $D_{\bullet} = 0.206008 \text{ days} = 4.944 \text{ hours}$

From the relation between the period of revolution and the distance we find that the distance corresponding to this period is  $R_0 = 9,214.0$  miles. Neglecting the eccentricity of the moon's orbit we found for the initial distance 9,194.4 miles.

But, as was explained in the preceding section, the initial eccentricity could not have been zero for the present eccentricity is different from zero. The larger it was the shorter the initial period and the smaller the initial distance. It will be a liberal assumption to suppose it was  $\epsilon_0 = 0.1$ , for then the initial perigee and apogee distances differed by 1,800 miles. With this value and putting D = P we find as the smaller root of the first equation of (98)  $D_0 = 0.205797d = 4.939$  hours. This corresponds to an initial mean distance of 9,207.7 miles, not differing materially from that found when the initial eccentricity was neglected.

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**XII.** CASE 
$$i \neq 0$$
  $i_1 \neq 0$   $a_2 = 0$   $e = 0$   $S = 0$ .

If i is to be taken different from zero and subject to change it is necessary to suppose that  $i_1$  may vary also, for all the interactions are mutual. In this case equations (9') become

$$M' = P^{\frac{1}{2}} \sin i \sin \Omega + \frac{m_1 \sin i_1 \sin \Omega_1}{D}$$

$$M'' = P^{\frac{1}{2}} \sin i \cos \Omega + \frac{m_1 \sin i_1 \cos \Omega_1}{D}$$
(114)

We may choose the xy-plane so that it shall coincide with the invariable plane of the system. Then M'=M''=0, and equations (114) give

$$\Omega_1 = \Omega + n\pi$$
  $(n = 0 \text{ or } 1)$ 

With this relation equations (114) become

$$\left[P^{\frac{1}{2}}\sin i\pm \frac{m_1\sin i_1}{D}\right]\sin \Omega = 0 \qquad \left[P^{\frac{1}{2}}\sin i\pm \frac{m_1\sin i_1}{D}\right]\cos \Omega = 0$$

whence

$$P^{i} \sin i \pm \frac{m_{1} \sin i_{1}}{D} = 0 \tag{115}$$

In this discussion we shall take D as essentially positive and let i and i, vary from 0 to  $\pi$ . Then we must take the lower of the two signs in (115), or  $\Omega_1 = \Omega + \pi$ . This equation and equations (9) and (10), under the hypotheses of this section, give us

$$0 = P^{\frac{1}{2}} \sin i - \frac{m_1 \sin i_1}{D}$$

$$M = P^{\frac{1}{2}} \cos i + \frac{m_1 \cos i_1}{D}$$

$$\frac{E}{\pi} = -\frac{1}{P^{\frac{1}{2}}} + \frac{m_1}{D^2}$$
(116)

Eliminating D and  $i_1$  from the last of these equations by means of the first two, we have

$$\frac{m_1 E}{\pi} = -\frac{m_1}{P^{\frac{1}{2}}} + P^{\frac{1}{2}} - 2M \cos i P^{\frac{1}{2}} + M^2$$

The conditions for a maximum or minimum of E considered as a function of i and P are

$$\frac{m_1}{\pi} \frac{\partial E}{\partial i} = 2MP^{\frac{1}{2}} \sin i = 0 \qquad \frac{m_1}{\pi} \frac{\partial E}{\partial P} = \frac{2}{3} \frac{m_1}{P^{\frac{1}{2}}} + \frac{2}{3} \frac{1}{P^{\frac{1}{2}}} - \frac{2}{3} \frac{M \cos i}{P^{\frac{1}{2}}} = 0$$

The first equation can be satisfied only by i=0 (the case  $i=\pi$  makes only a change in direction of the axes in the final solution). Then the second one gives, since P can not equal infinity, as the conditions for a maximum or a minimum

$$i=0$$
  $P^{i}-MP+m_{i}=0$  (117)

Then the first equation of (116) shows that either  $i_1=0$  or  $D=\infty$ . In the latter case  $i_1$  is indeterminate.

To investigate whether the roots of (117) correspond to a maximum or minimum we form (at i=0)

$$\frac{m_1}{\pi} \frac{\partial^2 E}{\partial i^2} = 2MP^{\frac{1}{2}} \qquad \frac{m_1}{\pi} \frac{\partial^2 E}{\partial i \partial P} = 0 \qquad \frac{m_1}{\pi} \frac{\partial^2 E}{\partial P^2} = \frac{2}{3} \frac{1}{P^{\frac{1}{2}}} \left(\frac{4}{3}P^{\frac{1}{2}} - M\right) \quad (118)$$

The right member of the first equation is positive for both roots of (117). We must consider the function

$$\frac{m_1^2}{\pi^2} \left[ \frac{\partial^2 E}{\partial t^2} \frac{\partial^2 E}{\partial P^2} - \left( \frac{\partial^2 E}{\partial t \partial P} \right)^2 \right] \equiv \frac{4M}{3P^4} \left( \frac{4}{3} P^4 - M \right)$$
(119)

For the smaller root of (117) the right member of this equation is negative, and therefore E is neither a maximum nor a minimum for this set of values. For the larger root of (117) it is positive and the corresponding value of E is a true minimum. Whenever the system arrives so near the condition corresponding to this point that the equi-energy curves are closed they remain closed for all smaller values of E down to the minimum, and under the influence of tidal friction the system will inevitably approach this condition of minimum E, and having attained it will remain there.

condition of minimum E, and having attained it will remain there. It follows from the second of (116) that for either value of P satisfying (117) we have D-P.

# XIII. APPLICATION OF CASE XII TO THE EARTH-MOON SYSTEM.

There is a difficulty in attempting to determine the position of the invariable plane of the earth-moon system, for the plane of the moon's orbit is continually changed by the perturbative action of the sun. In the course of about  $9\frac{1}{2}$  years the line of nodes of the moon's orbit makes a complete revolution, and the inclination of the plane of the earth's equator varies all the way from  $23.5^{\circ}+7^{\circ}$  to  $23.5^{\circ}-7^{\circ}$ . We shall suppose here that the sun is not disturbing the orbit of the moon, and that the inclination of its orbit to the plane of the ecliptic is zero. Let us take the plane of the ecliptic as the original xy-plane. Then the angle between the plane of the ecliptic and the invariable plane is given by

$$\cos i = \frac{M}{\sqrt{M^2 + M'^2 + M''^2}} = \frac{P^{\frac{1}{2}} + \frac{m_1}{D} \cos (23.5^{\circ})}{\sqrt{P^{\frac{3}{2}} + \frac{2m_1P^{\frac{1}{2}}}{D} \cos (23.5^{\circ}) + \frac{m_1^2}{D^2}}}$$
(120)

Since 
$$\Omega_1 = \Omega + \pi$$
 we have  $i_1 = 23.5^{\circ} - i$  (121)

In the case of the earth-moon system we find

$$i-4^{\circ}$$
  $i_1=19.5^{\circ}$  (122)

Then M of (116) becomes M=3.59654. With this value of M the smallest root of (117) is P=0.20852. This period corresponds to a distance of R=9,364 miles. However, the initial inclinations could not have been precisely zero, and consequently the initial distance must have been somewhat less than this amount. But the chief point of interest is that the factors neglected in the discussion of section V so far all make the initial distance greater than that found in that place.

**XIV.** CASE 
$$i=0$$
  $i_1=0$   $e=0$   $a_2=0$   $S \neq 0$ .

The sun affects the evolution of the earth-moon system in two ways. First, its direct perturbing influence on the moon makes the month longer than it would be if the moon were revolving at its present mean distance in an undisturbed orbit. In the second place the tides which the sun raises in the earth retard its rotation and reduce the moment of momentum of the earth-moon system. We shall consider these two influences separately.

The relation among the sum of the masses of the earth and moon, the mean distance from the earth to the moon, and the moon's period is found in the theory of the moon's motion to be

$$\frac{4\pi^2}{P^2}a^3\left[1+\frac{1}{2}\left(\frac{P}{P'}\right)^2....\right]=k^2(m_1+m_2)$$
 (123)

where P' is the length of the year. With this relation instead of having

$$\frac{4\pi^2a^3}{P^2} = k^2(m_1 + m_2)$$

equations (9) and (10) become, when  $e=i=i_1=a_2=0$ ,

$$M = P^{\frac{1}{2}} \left[ 1 - \frac{1}{3} \left( \frac{P}{P'} \right)^2 \dots \right] + \frac{m_1}{\overline{D}} \qquad \frac{E}{\pi} = -\frac{1}{P^{\frac{1}{2}}} \left[ 1 + \frac{2}{3} \left( \frac{P}{P'} \right)^2 \dots \right] + \frac{m_1}{\overline{D}^2}$$
 (124)

The disturbing forces which have made these changes in the equations are mostly radial, and so far as the radial components are concerned can not change the moment of momentum. The tangential components are periodic with equal and symmetrical positive and negative values in a period. Consequently the M will not have changed under these influences.

At the time of the supposed separation of the earth and moon P = D, and the first of (124) gives for the determination of P

$$P^{1}\left[1-\frac{1}{3}\left(\frac{P}{P'}\right)^{2}...\right]-MP+m_{1}=0$$
 (125)

We find from the first of (124) that the value of M is in this case M=3.63428. The smaller root of (125) for this value of M is  $P_0=0.205760$ , and this period corresponds to an initial distance of  $R_0=9,206.2$  miles, a little greater than that found when the sun's action was neglected.

Consider the direct tidal friction of the sun upon the earth-moon system. The sun's tides lengthen D without producing a corresponding change in the motion of the moon. Consequently in this case M is not constant.

Let us assume, as before, that the amount of tidal friction is directly proportional to the product of the square of the tide-raising force and the square of the velocity of the tidal wave along the earth. It also depends upon the physical condition of the earth. Then we have, including the tides produced by both the moon and the sun,

$$\frac{dE}{dt} = -C \left[ \frac{m_2^2}{r^6} \frac{(P-D)^2}{P^2 D^2} + \frac{S^2}{r'^6} \frac{(P'-D)^2}{P'^2 D^2} \right]$$
(126)

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where the first term comes from the tides raised by the moon and the second from the tides raised by the sun. Since E can only decrease, C must be positive. The factor of proportionality, C, is the same for both since it depends only upon the physical condition of the earth.

Substituting (126) in the second of (32) we have the rate of change of the day defined by

$$\frac{dD}{dt} = -\frac{C}{2m_1\pi} \frac{m_2^2}{r^6} \frac{D}{P} (P-D) \left\{ 1 + \left(\frac{r}{r'}\right)^6 \left(\frac{S}{m_2}\right)^2 \left(\frac{P'-D}{P-D}\right)^2 \left(\frac{P}{P'}\right)^2 \right\} (127)$$

The length of the month is changed by the moon's tides alone, and bears a definite relation to the rate of change of the day due to the moon's tides. From (32) this relation is found to be

$$\frac{3m_1}{D^2}\frac{dD}{dt} = \frac{1}{P^{\frac{3}{2}}}\frac{dP}{dt}$$

When the sun's action on the rotation of the earth is included we have therefore

$$\frac{3m_1}{D^2}\frac{dD}{dt} = \frac{1}{P^2} \left\{ 1 + \left(\frac{r}{r'}\right)^6 \left(\frac{S}{m_2}\right)^2 \left(\frac{P' - D}{P - D}\right)^2 \left(\frac{P}{P'}\right)^2 \right\} \frac{dP}{dt}$$
 (128)

From the formulas for the month and year we have

$$\left(\frac{r}{r'}\right)^{6} = \left(\frac{m_1 + m_2}{S + m_1 + m_2}\right)^{2} \left(\frac{P}{P'}\right)^{4}$$

Since  $m_1$  is large compared to  $m_2$ , and S is large compared to  $m_1$ , this relation becomes with sufficient approximation

$$\left(\frac{r}{r'}\right)^{4} = \left(\frac{m_1}{S}\right)^{2} \left(\frac{P}{P'}\right)^{4}$$

Then equation (128) becomes

$$\frac{3m_1}{D^2}\frac{dD}{dt} = \frac{1}{P^{\frac{1}{2}}} \left\{ 1 + \left(\frac{m_1}{m_2}\right)^2 \left(\frac{P' - D}{P - D}\right)^2 \left(\frac{P}{P'}\right)^6 \right\} \frac{dP}{dt} \tag{129}$$

If we integrate this equation and determine the constant of integration by the present values of P and D, and if we then put P-D and solve, we shall have as one of the roots the value of P at the time of the supposed separation of the earth and moon. But P and D enter this equation in such a complicated manner that it is not possible to express its solution in finite terms. The critical values of the variables are

$$P=0$$
  $D=0$   $P-D=0$   $1+\left(\frac{m_1}{m_2}\right)^2\left(\frac{P'-D}{P-D}\right)^2\left(\frac{P}{P'}\right)^6=0$ 

Only the third of these critical values will arise in the applications which will be made here.

In the present condition of the earth-moon system we find that

$$\left(\frac{m_1}{m_2}\right)^2 \left(\frac{P'-D}{P-D}\right)^2 \left(\frac{P}{P'}\right)^6 = 0.224$$

It will appear in the computations which follow that as P and D decrease in such a way as continually to satisfy (129), this function decreases rapidly until P=0.25 and D=0.25 approximately. For  $1 \ge D > 0.25$  it is convenient for the purpose of solving (129) to let

$$Q = \frac{m_1}{D} + P^{\frac{1}{2}} - M \tag{130}$$

With this substitution equation (129) becomes

$$\frac{dQ}{dt} = -\frac{1}{3} \left(\frac{m_1}{m_2}\right)^2 \frac{1}{P^{\frac{1}{2}}} \left(\frac{P' - D}{P - D}\right)^2 \left(\frac{P}{P'}\right)^6 \frac{dP}{dt}$$
 (131)

If we should eliminate D from (131) by means of (130) the result would have the form

$$\frac{dQ}{dP} = F(P, Q) \tag{132}$$

If we let  $P_0$  represent the present value of P, and M the total present moment of momentum of the earth-moon system, then at  $P = P_0$  we have Q = 0, and an approximate solution of (132) is

$$Q_1 = \int_{P_2}^{P} F(P,0) dP$$
 (133)

Successive approximations may be found by the series of operations

$$Q_{2} = \int_{P_{0}}^{P} F(P, Q_{1}) dP \qquad Q_{3} = \int_{P_{0}}^{P} F(P, Q_{2}) dP \dots$$

$$Q_{n} = \int_{P_{0}}^{P} F(P, Q_{n-1}) dP \qquad Q_{n+1} = \int_{P_{0}}^{P} F(P, Q_{n}) dP \dots$$

This series of approximations approaches the true value of the integral provided the upper limit does not pass beyond a point for which F(P,Q) has a singularity. In the application of these formulas we are explicitly limiting ourselves to a region in which F(P,Q) is everywhere regular. The integrations can be very easily carried out by mechanical quadratures to the desired degree of accuracy.

Since we wish to trace the system back and find for what values of P and D the two variables were equal, we must take  $P < P_0$  in the integration.

<sup>&</sup>lt;sup>1</sup> Picard, Traité d'Analyse, vol. 2, pp. 301-304.

When the integration has been carried so far back that P-D is small enough to make the second term in the right member of (129) the dominant one, it is convenient to change from P to D as the independent variable of integration. We may now write (129) in the form

$$\frac{dP}{dD} = f(P, D) = \frac{3m_1(P-D)^2 P^{\frac{3}{2}}}{D^2 \left[ (P-D)^2 + \left(\frac{m_1}{m_2}\right)^2 (P'-D)^2 \left(\frac{P}{P'}\right)^{\frac{3}{2}} \right]}$$
(134)

For P-D=0 this equation does not have a singular point when D is the independent variable, for at this point f(P,D) vanishes.

independent variable, for at this point f(P, D) vanishes. Suppose corresponding values of P and D have been found by (132) and (130) until  $P_0$  and  $D_0$  are obtained, and that their difference is small. Then P may be expressed in terms of D by an expression of the form

$$P - P_0 = \sum_{i=1}^{\infty} A_i (D - D_0)^i$$
 (135)

provided the modulus of  $D-D_0$  is sufficiently small. Substituting (135) in (134), expanding the right member, and equating coefficients of corresponding powers of  $D-D_0$ , we find

$$A_1 = f(P_0, D_0)$$
  $2A_2 = A_1 \frac{\partial f(P_0, D_0)}{\partial P_0} + \frac{\partial f(P_0, D_0)}{\partial D_0} \dots$  (136)

where

$$\begin{split} A_1 &= \frac{3m_1(P_0 - D_0)^2 P_0^{\frac{1}{2}}}{D_0^2 \left[ (P_0 - D_0)^2 + \left( \frac{m_1}{m_2} \right)^2 (P' - D_0)^2 \left( \frac{P_0}{P'} \right)^{\frac{1}{2}} \right]} \\ &\frac{\partial f\left( P_0, D_0 \right)}{\partial P_0} &= \frac{2m_1(P_0 - D_0) \left( 4P_0 - D_0 \right)}{P_0^{\frac{1}{2}} D_0^2 \left[ (P_0 - D_0)^2 + \left( \frac{m_1}{m_2} \right)^2 (P' - D_0)^2 \left( \frac{P_0}{P'} \right)^{\frac{1}{2}} \right]} \\ &- \frac{6m_1(P_0 - D_0)^2 P_0^{\frac{1}{2}} \left[ P_0 - D_0 + 3 \left( \frac{m_1}{m_2} \right)^2 (P' - D_0)^2 \frac{P_0^{\frac{1}{2}}}{P'^{\frac{1}{2}}} \right]}{D_0^2 \left[ (P_0 - D_0)^2 + \left( \frac{m_1}{m_2} \right)^2 (P' - D_0)^2 \left( \frac{P_0}{P'} \right)^{\frac{1}{2}} \right]} \end{split}$$

Therefore

$$\begin{split} A_{3} &= -\frac{P_{0}}{D_{0}(P_{0} - D_{0})} A_{1} + \frac{1}{3} \frac{(4P_{0} - D_{0})}{P_{0}(P_{0} - D_{0})} A_{1}^{2} \\ &+ \frac{\left[P_{0} - D_{0} + \left(\frac{m_{1}}{m_{2}}\right)^{2} (P' - D_{0}) \left(\frac{P_{0}}{P'}\right)^{6}\right]}{\left[(P_{0} - D_{0})^{2} + \left(\frac{m_{1}}{m_{2}}\right)^{2} (P' - D_{0})^{2} \left(\frac{P_{0}}{P'}\right)^{6}\right]} A_{1} \\ &- \frac{\left[P_{0} - D_{0} + 3 \left(\frac{m_{1}}{m_{2}}\right)^{2} (P' - D_{0})^{2} \frac{P_{0}^{6}}{P'^{6}}\right]}{\left[(P_{0} - D_{0})^{2} + \left(\frac{m_{1}}{m_{2}}\right)^{2} (P' - D_{0})^{2} \left(\frac{P_{0}}{P'}\right)^{6}\right]} A_{1}^{2} \end{split}$$

Since these equations are applied only when  $P_0 - D_0$  is small and  $D^0$  small compared to P', we have approximately

$$A_{1} = \frac{3m_{2}^{2} (P_{0} - D_{0})^{2} P^{4}}{m_{1} D_{0}^{2} P_{0}^{\frac{15}{2}}}$$

$$A_{2} = -\frac{3m_{2}^{2} (P_{0} - D_{0}) P^{4}}{m_{1} D_{0}^{3} P_{0}^{\frac{15}{2}}} - \frac{3m_{2}^{2} (P_{0} - D_{0})^{3} (5P_{0} - 8D_{0}) P^{6}}{m_{1}^{2} D_{0}^{4} P_{0}^{\frac{15}{2}}}$$

$$= -\frac{P_{0}}{D_{0} (P_{0} - D_{0})} A_{1} - \frac{(5P_{0} - 8D_{0})}{3P_{0} (P_{0} - D_{0})} A_{1}^{2}$$

$$(137)$$

By successive application of (135) and (137) the corresponding values of P and D can be followed until P-D passes through zero. The value of P, for which P-D, can then be determined by interpolation. The corresponding values of P and D in the following table have been computed from equations (130), (131), (135) and (137). The third column gives  $\rho$ , the ratio of the rate of the change in the rotation of the earth due to the sun's tides to that due to the moon's tides.

P	D	P
27.32166	0.99726	0.224
25.32166	0.86685	0.165
23.32166	0.76672	0.119
21.32166	0.68644	0.083
19.32166	0.61939	0.056
17.32166	0.56278	0.036
15.32166	0.51291	0.022
13.32166 11.32166	0.46847 0.42786	0.013
9.32166	0.39012	0.003
7.32166	0.35410	0.001
5.32166 3.32166	0.31875 0.28229	0.000
1.32166	0.23966	0.000
0.20037	0.20037	∞

The initial common period of rotation and revolution is found by this computation to be 0.20037 day, corresponding to a distance of 9,045 miles.

This is 149 miles less than that found when the action of the sun's tides upon the rotation of the earth was neglected. That is, when the effects of the sun's tides upon the rotation of the earth are included, it is found that the possible initial distance of the moon is not materially diminished, and that the theory of the fission of the earth and moon is still subject to the serious embarrassment of wide separation immediately after the supposed division into distinct masses.

## XV. THE SECULAR ACCELERATION OF THE MOON'S MEAN MOTION.

As is well known, there is a secular acceleration of the moon's mean motion of about 4" per century which has not been explained by the ordinary perturbation theory. It was long ago suggested by Delaunay that it may be due to tidal friction, and Darwin has made an investigation of the subject in 2, section 14.

If we accept the tidal explanation, the apparent acceleration of 4'' is due to an actual retardation of the moon, the only result possible according to (32), and a greater retardation of the rotation of the earth. Since the rotation of the earth is used to measure time, the period of revolution of the moon on this basis apparently is accelerated. In making the discussion we shall neglect the effects of  $a_2$ , e,  $i_1$ ,  $i_2$  and S.

Let  $-\triangle v_1$  be the gain in longitude of the moon in a century, and  $-\triangle v_2$  the corresponding gain in the angular distance of rotation of a meridian of the earth. Then we have

$$\frac{\Delta v_{2} - \Delta v_{1} = 4''}{dt} = -\frac{2\pi}{\theta^{2}} \frac{d\theta}{dt} = \frac{2\pi}{\theta^{2}} \frac{\Delta v_{1}}{(100P')^{2}} = \frac{P^{2}}{2\pi} \frac{\Delta v_{1}}{(100P')^{2}}$$

$$\frac{dD}{dt} = -\frac{2\pi}{\omega^{2}} \frac{d\omega}{dt} = \frac{2\pi}{\omega^{2}} \frac{\Delta v_{2}}{(100P')^{2}} = \frac{D^{2}}{2\pi} \frac{\Delta v_{2}}{(100P')^{2}}$$
(138)

From these equations and (32) we find

$$\frac{dD}{dt} = \frac{P^{\frac{1}{2}}D^{2}}{2\pi (P^{\frac{1}{2}} - 3m_{1})} \frac{4''}{(100P')^{2}} \qquad \frac{dP}{dt} = \frac{3m_{1}P^{2}}{2\pi (P^{\frac{1}{2}} - 3m_{1})} \frac{4''}{(100P')^{2}}$$
(139)

Representing the value of P at  $t-t_0$  by  $P_0$ , integrating the second equation, and determining the constant of integration, we have

$$P^{\frac{1}{2}} - P_{\bullet}^{\frac{1}{2}} + m_1 \left(\frac{1}{P} - \frac{1}{P_{\bullet}}\right) = \frac{m_1}{2\pi} \frac{4''}{(100P')^2} (t - t_{\bullet})$$
 (140)

The present rate of tidal evolution of the earth-moon system depends upon the forces acting and upon the physical condition of these bodies. If we regard the 4" per century of apparent gain in longitude of the moon as due to tidal evolution, we have a measure of the  $\frac{dE}{dt}$  of equations (32).

We may use equation (140) to compute the time  $(t-t_0)$  corresponding to any value of P provided the physical condition of the system, and particularly that of the earth, has not changed sensibly in the mean time. data furnished by geology are showing more and more that the earth has been sensibly in its present state, except for approximately periodic oscillations in its climate, for many millions of years. For the purposes of computation we shall assume that it has been indefinitely so. While this assumption is not strictly true, the actual observational data show that it is almost certainly much less in error than the assumption, stimulated by the Laplacian theory of the origin of the earth, that our planet was fluid in the not very remote past. Remembering the fact that we are assuming simply that the apparent secular acceleration of the moon's mean motion is due to tidal friction and that it is a measure of the rate of tidal evolution, and that we are assuming further that the physical condition of the earth and moon has not changed in the time covered by our calculations, we find from (23) that when D=20 hours the value of P was 24.096 days, and from (140) that P had this value 220,700,000,000 years ago. If the action of the sun had been included the interval would have been decreased by about 20 per cent. It is impossible to believe that the neglected factors, such as the eccentricity and inclination of the moon's orbit, could reduce the time enough to change the order of these results. This computation, which has the merit of being based quantitatively on actual observations, points very strongly to the conclusion that tidal evolution is so slow a process that it can not have played an important rôle in the earth-moon system, even when we consider an interval of a billion years.

There is, however, another possibility that may be considered. least conceivable that there may be unknown forces acting upon the earthmoon system in such a way that they largely mask the relative secular tidal acceleration of the moon. Any thing increasing the moon's distance and period without otherwise disturbing its motion, or any thing accelerating the rotation of the earth, would tend to offset the secular acceleration produced by tidal friction. The possible secular contraction of the earth is a factor working in the right direction. But from the numbers obtained above it follows that, if we are to escape from the conclusion that tidal friction is now a negligible factor, we must assume that the actual relative tidal acceleration of the moon is several hundreds of times 4" per century. Supposing the reduction to 4" is due to the acceleration of the rotation of the earth because of shrinking, it follows that at every epoch in the past the day and the month were more nearly equal than they would have been except for this factor. Finally, at the limit at which they were equal, their common period was many times that computed above, and their great initial distance fatal to the fission theory. If there are unknown forces retarding the moon's revolution, the conclusions are the same.

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#### XVI. SUMMARY.

The object of this investigation has been to examine the theory of tidal evolution in order to find out, if possible, not what might take place under certain assumed conditions, but how important this process has been in the actual development of our system. The aim has been to avoid, as far as possible, assumptions regarding the uncertain factors depending upon the physical conditions of the bodies involved. In order to compare the theory with the actual facts the various methods of testing it have been carried to quantitative results.

A large part of the discussion has been made to depend upon the components of the moment of momentum and upon the energy of the system. In section II the moment of momentum equations and the energy equation are developed, and they are perfectly rigorous so long as the two bodies are subject to no forces except their mutual attraction. Under this condition the three components of moment of momentum are rigorously constant, and the three equations which express these conditions are fixed relations among the various quantities which define the dynamical state of the system. The energy equation is a relation among the same quantities, but unlike the components of the moment of momentum the energy diminishes by friction. These relations are too few to determine the changes which will actually take place, but they give important information about them. They are particularly valuable, for they are true whatever the physical conditions of the bodies involved.

One of the conclusions reached by Darwin was that it is probable that the earth and moon have developed from an original mass by fission. One critical test of this hypothesis is the determination of the smallest distance at which the bodies could have revolved around each other consistently with the present moment of momentum and energy. This test has been worked out quantitatively, first with the problem simplified so that the conclusions are absolutely certain under the hypotheses; then the effects of various modifying conditions, which seem more or less probable, have been examined, one after another, and their influence upon the final result determined. The results reached are so near the border line separating what is favorable to the theory from that which is unfavorable, that it is important in applying this test to determine accurately the constants upon which the system depends. One of these is the rotational moment of momentum of the earth, which depends only upon the law of density of the earth as an uncertain factor. In section III the constants of the density according to the Laplacian law are worked out. It is found that according to this law the density varies from 2.75 at the surface to 10.84 at the center. While this is probably not an exact expression for the earth's density, the inherent probabilities as well as the actually observed precessional phenomena lead us to conclude that it is not sensibly in error for the purposes of this discussion. By the same law the surface and central densities of the moon are respectively 1.65 and 6.51.

In section IV the moment of inertia for the Laplacian law of density is found, and it comes out 0.336 times the mass instead of 0.4 times the mass, as in the case of a homogeneous body.

Section V is devoted to a consideration of the problem in which the two bodies revolve in circular orbits undisturbed by exterior forces, and in which the rotational moment of momentum and energy of one of the bodies are so small that they may be neglected, while the axis of rotation of Although the condithe other is perpendicular to the plane of the orbit. tions assumed in this section are not exactly fulfilled in any physical problem, still they are near enough those prevailing in the earth-moon system to throw much light on what may possibly have taken place. But the chief value of this investigation is that the variables are so few that the results are precise, except as to the time rate at which the possible changes will take place. The thing of greatest interest is that the rates of change of revolution and rotation are proportional to the rate of the loss of energy through friction, and are not directly dependent upon the phases and lags of the tides or the surface peculiarities of the tidally distorted body. These results show that, so far as the hypotheses upon which they are founded apply to the earth-moon system, if we could from the direct tidal observations calculate the rate of loss of energy in tides raised by the moon upon the earth, then we could compute the rate of tidal evolution at the present time. While this problem undoubtedly presents serious difficulties, they are not more formidable than those of assigning to the earth a physical constitution which shall agree reasonably with the truth.

Assuming that friction is proportional to the height of the tide and its velocity relative to the surface of the tidally distorted body, and that the loss of energy is proportional to the square of the friction, equations are developed, (33), giving the rates of change of the periods of revolution and rotation. They involve only one unknown constant depending upon the physical constitution of the distorted body.

In section VI the equations of section V are applied to the earth-The influence of the sun is neglected, later computation moon system. showing that its effects upon the rotation of the earth are now about onefifth as great as the moon's. The rotational moment of momentum and energy of the moon are small because of the small mass of the moon, its small dimensions, and its slow rotation. Using the numerical data, it is found that the moon's rotational moment of momentum is less than one thirty-thousandth that of the earth. Since the eccentricity of the moon's orbit is small and the cosine of obliquity of the ecliptic not much less than unity, it is seen that the conditions of this investigation really approximate rather closely to the actual earth-moon system. It is found that the month has always been increasing and that it can not pass beyond 47.7 of our present days, at which period the month and day will be equal and the system move as a rigid body. There is no way of telling by this investigation how long a time will be required for the system to reach that state. But it is a more interesting fact that the month can never have been less than 4.93 of our present hours, this being the period of revolution when the distance from the center of the earth to the center of the moon was 9,194 miles. Consequently we must suppose that when the moon broke off from the earth it was at this distance from it, or 5,236 miles from its present surface. Or, including the radius of the moon and supposing that BUMMARY. 129

both the earth and moon were of the same density and shape as at present, the distance from the surface of one body to the surface of the other was immediately after fission 4,155 miles. Since this result is altogether incompatible with the obvious implications of the fission theory, we must either abandon the theory or show that this number would be very largely reduced by including the effects of the neglected factors. Consequently we examine the effects of various neglected conditions and influences.

If the earth were rotating in 4.93 of our present hours it must obviously have been very oblate instead of spherical as was assumed in the computation. In the absence of certain knowledge we may assume that its equatorial radius reached out to the surface of the moon when the distance of its center was 9,194 miles, that the oblateness was such that the volume was the same as at present, and that the law of density was such that its rotational moment of momentum was the same as it would have been if it were spherical and the Laplacian law of density prevailed. We find that under these hypotheses the polar radius would have been only 942 miles. A scale drawing shows that this oblateness is out of the question, and a little consideration shows that the equatorial zone must have been so rare as to make it impossible to account for the mass of the moon.

If we waive the condition that for a given period of rotation the law of density was such as to keep the rotational moment of momentum the same as when the body was supposed to be a sphere, we shall have to suppose the moment of momentum was greater than this in order to get sufficient matter in the periphery to account for the origin of the moon. But this supposition leads to the conclusion that the nearest possible distance of the moon was greater than the 9,194 miles found before.

Another hypothesis is that the earth was initially larger than at present, and has shrunk to its present dimensions as it cooled. It was found in this case also that the initial distance of the moon must have been greater than the 9,194 miles found on the original hypothesis.

An examination was made of the hypothesis that the earth originally had a radius of 9,194 miles and a density such as to keep its moment of momentum the same as if it were of its present size. It was supposed the density varied according to the Laplacian law and the constants of the law were worked out by the conditions of the hypotheses. It turned out that the density of the surface must have been negative, a result having no physical interpretation and proving the falsity of at least one of the hypotheses upon which the computations were made.

In sections VII and VIII the problem was treated without neglecting the rotational moment of momentum and energy of the moon, but keeping the earth and moon spherical. It turned out that the initial distance of the earth and moon could not have been less than 9,200 miles. That is, when this factor is included the result becomes less favorable to the fission theory than when it was omitted.

Then in sections X and XI the hypothesis was made that the moon's rotational moment of momentum and energy may be neglected, but the eccentricity of the moon's orbit was given the value assigned by observations. It was found under these hypotheses that the initial distance of the

moon could not have been less than 9,214 miles, a result more unfavorable to the fission theory than that obtained when the eccentricity of the moon's orbit was neglected.

In sections XII and XIII it was assumed that the rotational moment of momentum and energy of the moon and eccentricity of the moon's orbit may be neglected, but the inclination of the plane of the earth's equator to the plane of the moon's orbit was taken into account. Under these hypotheses it was found that the initial distance of the moon could not have been less than 9,364 miles, a result more unfavorable to the fission theory than any of those heretofore derived.

All of the factors initially neglected and later taken up one by one have made the initial distance greater than the originally computed 9,194 miles. Obviously all of them combined would operate in the same direction. Since they only increase a difficulty which was in the first place serious, it is not necessary to go to numerical results for all of them combined.

The factors which remain to be considered in attempting to test the fission theory by computing the initial distance of the moon are the sun's perturbations of the moon's orbit and its effect upon the rotation of the earth. The first part of section XIII is devoted to a discussion of the direct action of the sun upon the moon's orbit, and it is shown there that including this influence alone the initial distance of the moon could not have been less than 9,206 miles, which is somewhat greater than that found when the sun's action was neglected.

The second part of section XIII treats the relative retardative effects of the sun upon the rotation of the earth. The magnitude of the tideraising force of the sun compared to that of the moon can easily be computed. Other things being equal there are good grounds for assuming that the rate of tidal evolution is proportional to the square of the tide-raising force. The friction depends also upon the speeds of the tidal waves with respect to the earth's surface. At the present time the speeds of the moon's and the sun's tides are about equal, but if we trace the system back until the month and day were approximately equal this relation is no longer approximately verified. We must resort, therefore, to some specific assumption as to the way in which tidal friction depends upon the speeds of the tides over the surface of the earth. The assumption was made that friction is proportional to the first power of the velocity, and therefore that the loss of energy is proportional to the second power of the velocity. practically certain that this assumption will give results which are sensibly Using this hypothesis and supposing that the rotational moment of momentum and energy of the moon, the eccentricity of the moon's orbit, the inclination of the plane of the earth's equator to the plane of the moon's orbit, and the direct action of the sun on the moon's orbit may all be neglected, it was found that the initial distance of the moon was Thus it is seen that the one reduced from 9,194 miles to 9,045 miles. factor which makes the moon's initial distance less than that found in the first computation is not only of no particular consequence, but also that it is less than some of the factors which increase it. Using all those factors whose effects have been computed when they have been supposed to act

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separately, and supposing that they would be essentially the same when acting jointly, we find that the smallest possible distance of the moon compatible with present conditions is 9,241 miles. Fig. 16 shows the earth and moon and their initial distance to scale, and obviously one would need extremely strong confirmatory evidence to convince him that the moon had just broken off from the earth. The distance from the surface of the earth to the surface of the moon is 4,201 miles, or 243 miles greater than the radius of the earth.

As a concession to the theory, we may assume that the earth and moon have separated by fission so that their periods of rotation and revolution are precisely equal, and then inquire whether the present system could develop from it. If the original orbit were exactly circular the orbit would always remain circular. Since the moon's orbit now has considerable eccentricity it follows that we must assume that the orbit immediately after separation was somewhat eccentric. But since the rotations would be sensibly uniform while the revolution would be such as to fulfil the law





Fig. 16.

of areas, there would be relative motion of the various parts and therefore tidal evolution. The question whether this friction would drive the moon farther from the earth or bring it back and precipitate it again upon the earth is treated in section X, and it is found there, under the assumption that the loss of energy is proportional to the square of the tide-raising force and the square of the velocity of the tide along the surface of the earth, that the tides would bring the moon again to the earth. Thus, unless some of the neglected factors can offset this result, the direct implications of the theory destroy it, and it may be noted here that these remarks apply with equal force to the hypothesis that the binary stars have originated by fission and that their present distances from each other and the eccentricities of their orbits are a result of tidal friction.

If we neglect the rotational moment of momentum and energy of the moon, the eccentricity of the moon's orbit, and the inclination of the plane of the earth's equator to the plane of the moon's orbit, then it is certain, as was shown in sections V and VI, that tidal friction will at the present time lengthen both the day and the month, but at such relative rates that the number of days in a month will decrease. Consequently if time be measured by the rotation of the earth the moon will continually get ahead of its place,

as predicted by the gravitational theory neglecting tidal evolution. This relative gain in longitude, if established by observations, will give us the measure of the rate of tidal evolution at the present time, and we can safely apply it, by properly varying the factors depending upon the moon's distance, over any interval during which the physical condition of the earth has been essentially as it is at present. Since the geological data go to show that the physical state of the earth has been about as it is now for many tens of millions of years, and do not give certain evidences of any radically different general physical conditions, we are perhaps justified in boldly applying results based on the present rate of gain of the moon for a very long interval of time.

It is well known that a comparison of ancient and modern eclipses shows that the moon has an acceleration in longitude of about 4" per century which is not explained by perturbations. Let us assume that this is due to tidal friction and is the measure of it at the present time. At this rate it will take over 30,000,000 years for the moon to gain one revolution. Consequently we see without any computation that it must have been an extremely long time in the past when its period was a small fraction of its present period.

The problem was treated in section XV, and it was found there that, if the physical condition of the earth has been essentially constant, the length of the day was 20 of our present hours, and of the month, 24 of our present days not less than 220,000,000,000 years ago. It is extremely improbable that the neglected factors, such as the eccentricity of the moon's orbit, could change these figures enough to be of any consequence. This remarkable result has the great merit of resting upon but few assumptions and in depending for its quantitative character upon the actual observations. If it is accepted as being correct as to its general order, it shows that tidal evolution has not affected the rotation of the earth much in the period during which the earth has heretofore been supposed to have existed even by those who have been most extravagant in their demands for time. And if one does not accept these results as to their general quantitative order, he faces the embarrassing problem of bringing his ideas into harmony with the observations.

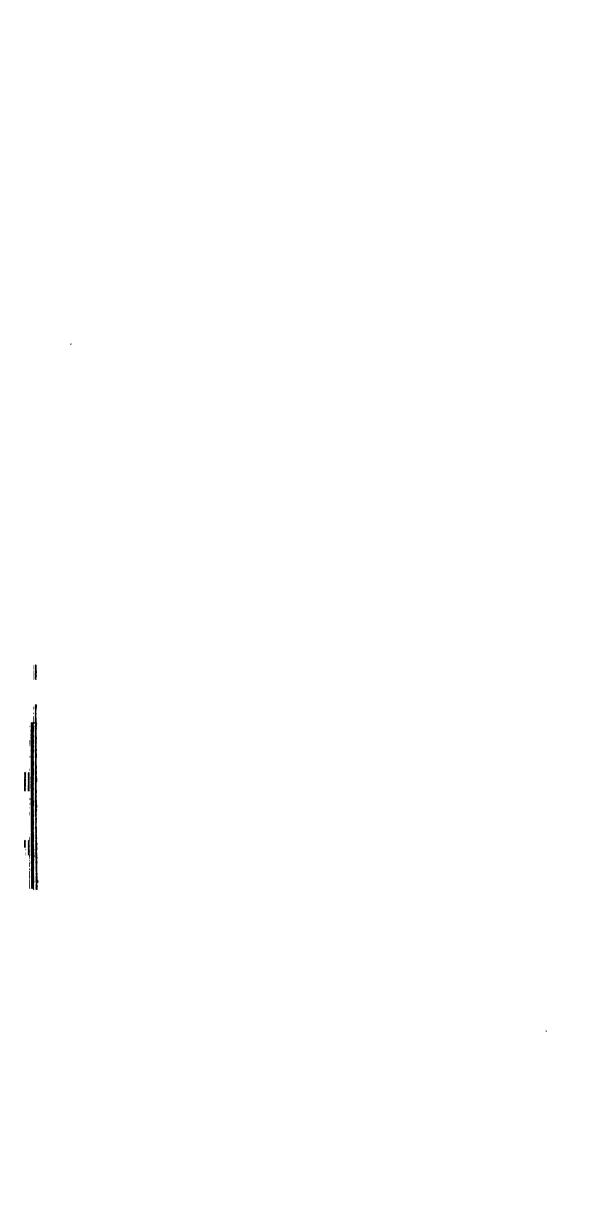
If tidal friction has been an important factor in the evolution of the earth-moon system, then presumably it has also been an important factor somewhere else in the universe. Certainly one would expect to find the theory encountering no difficulties in the case of any other planet. But the place where it has been applied most is in the orbits of the binary stars, which have been supposed to have become binaries through fission and to have become widely separated as a consequence of tidal evolution. The first difficulty is, as has been pointed out, that there must have been an initial eccentricity of the relative orbit, and this eccentricity would cause the bodies to reunite as a consequence of tidal friction. But there is another important difficulty, as was explained in section IX. If we suppose the binary to be composed of two equal suns moving just after separation as a rigid body, and if we waive the effects of the eccentricity for the sake of the argument, we find that there is a maximum distance to which the

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bodies can be driven from each other as a consequence of tidal friction, this maximum distance corresponding to a minimum of energy, and that this maximum distance is not many times greater than the distance immediately after separation. In particular, when the equations were applied to two stars each equal in mass and dimensions to the sun at an initial distance between centers of 866,000 miles, it was found, on the basis of conclusive reasoning, that the greatest distance possible as a result of tidal evolution would be only 1,042,400 miles. These results, which were obtained under the hypothesis that the stars suffered no shrinkage with loss of heat, were not radically modified when they were supposed to shrink to any extent whatever. The conclusion is that the widely separated binaries which our telescopes reveal to us can not have originated by fission, at least from masses condensed beyond the nebulous stage.

In a word, the quantitative results obtained in this paper are on the whole strongly adverse to the theory that the earth and moon have developed by fission from an original mass, and that tidal friction has been an important factor in their evolution. Indeed, they are so uniformly contradictory to its implications as to bring it into serious question, if not to compel us to cease to consider it as even a possibility.

<sup>&</sup>lt;sup>1</sup> This of course refers only to spontaneous fission without the accession of moment of momentum from some outside body.



CONTRIBUTIONS TO COSMOGONY AND THE FUNDAMENTAL PROPLEMS OF GEOLOGY			
	CANTEITITIANS:	AND THE PHNDAMENTAL	. DRARIEMS AF GRAIAGY

# NOTES ON THE POSSIBILITY OF FISSION OF A CONTRACTING ROTATING FLUID MASS

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## NOTES ON THE POSSIBILITY OF FISSION OF A CONTRACTING ROTATING FLUID MASS.

#### I. INTRODUCTION.

In the speculations on cosmogony there are two fairly definite hypotheses as to the manner in which a single body may give rise to two or more distinct masses without the intervention of external agencies. The first, as outlined by Laplace, is that possibly a rotating fluid may abandon an equatorial ring, which will subsequently be brought by its self-gravitation into an approximately spherical mass. The second, the fission theory, had its rise in Darwin's researches on tidal evolution, and in his speculations on the origin of the moon. It has found extensive application in attempts at explaining the great abundance of binary stars.

The hypothesis of Laplace has the support of no observational evidence. unless we regard the rings of Saturn as such, and rests upon no well-elaborated theory. On the contrary, there are well-known considerations of the moment of momentum of our system which compel us to reject it as being an unsatisfactory hypothesis for the explanation of the development of the planets. But the fission theory of Darwin, even if the origin of the moon is left aside as being doubtful, has strong claims for attention because of its immediate application to explaining the origin of spectroscopic and visual binaries and certain classes of variable stars. Besides, it is in a general way confirmed by the investigations of Maclaurin, Jacobi, Kelvin, Poincaré, and Darwin on the figures of equilibrium of rotating homogeneous fluids, and on their stabilities. In particular, considering a series of homogeneous fluid masses of the same density but of different rates of rotation it is shown that there is a continuous series of figures of stable equilibrium beginning with the sphere for zero rate of rotation; then, with increasing rotation, passing along a line of oblate spheroids until a certain rate of rotation is reached; then, with decreasing rate of rotation but with increasing moment of momentum, branching to a series of ellipsoids with three unequal axes, and continuing until a certain elongation is reached; and finally, at this point, branching to a series of so-called pear-shaped figures. It has been conjectured that if it were possible to follow the pear-shaped figures sufficiently far, it would be found that they would eventually reach a point where they would separate into two distinct masses. From this line of reasoning it has been regarded as probable that celestial masses, through loss of heat and consequent contraction, do break up in this way often enough to make the process an important one in cosmogony.

Aside from the unanswered question as to what form the pear-shaped figures finally lead, there are two reasons for being cautious in accepting the conclusions. One is that the celestial masses are by no means homogene-

ous. When they have reached, or are in, that condition of steady motion of slow rotation postulated in the investigation, they are undoubtedly always strongly condensed toward their centers. The other, and probably more important, one is that isolated celestial masses do not change their rates of rotation except when they change their densities or distribution of densities. While the theoretical discussions to which reference has been made regard the rate of rotation as the single variable parameter, in the actual case there is a corresponding change in density. The importance of not neglecting the latter is easily seen.

Consider a slowly rotating homogeneous fluid having the form of a nearly spherical oblate spheroid. The eccentricity of a meridian section depends  $\omega^2$ upon the quantity  $\frac{\omega}{2\pi k^2 \sigma}$ , where  $\omega$  is the angular rate of rotation,  $k^2$  the gravitational constant, and  $\sigma$  the density of the mass. The eccentricity of the axial section increases with the increase of this function, provided it does not go beyond a certain maximum. Now suppose the mass contracts in such a way as to remain homogeneous throughout, and so that it continues to rotate as a solid spheroid of equilibrium. Because the moment of momentum of an isolated mass is constant, the contraction implies an increase in w, and therefore, as far as this factor alone is concerned, an increase in the oblateness of the mass. But the contraction also implies an increase in  $\sigma$ , and therefore, so far as this factor alone is concerned, a decrease in the oblateness of the mass. That is, keeping the moment of momentum constant, as the dynamical situation requires, we find the eccentricity acted upon by two opposing factors. If, under the influence of these factors, the figure should become less oblate, the fission theory would get no support from the discussion; if it should get more oblate, the question is at what rate the mass must rotate and to what extent the contraction must proceed before there is a possibility of fission. This paper will be devoted to a brief discussion of these questions.

#### II. THE ELLIPSOIDAL FIGURES OF EQUILIBRIUM OF ROTATING HOMOGENEOUS FLUIDS.

For the applications which follow it will be necessary to review briefly the facts regarding the spheroidal and ellipsoidal figures of equilibrium and their conditions of stability.

Maclaurin<sup>1</sup> has shown that for very small values of  $\frac{\omega^{-}}{2\pi k^{2}\sigma}$  there are two ellipsoids of revolution which are figures of equilibrium, one of them being nearly spherical and the other very oblate, the limits for  $\omega = 0$  being respectively the sphere and infinite plane. For greater values of this quantity, the figure corresponding to the former is more oblate and that corresponding to the latter is less oblate. For  $\frac{\omega^2}{2\pi k^2 \sigma} = 0.22467$  . . . the two figures are identical. For  $\frac{\omega^2}{2\pi k^2 \sigma} > 0.22467$  . . . there is no ellipsoid of  $\omega^2$ revolution which is a figure of equilibrium.

Jacobi has shown<sup>2</sup> that if  $\frac{\omega^2}{2\pi k^2 \sigma}$  < 0.18709 . . . there is an ellipsoid of three unequal axes satisfying the conditions for equilibrium. When this quantity is very small, the axis of rotation and one other are very short and nearly equal to each other, while the third is relatively very long. With greater values of this quantity the shorter axes are longer and the longest axis is shorter. For  $\frac{\omega^2}{2\pi k^2 \sigma} = 0.18709$  . . . the figure becomes an ellipsoid of revolution and is identical with the more nearly spherical Maclaurin For  $\frac{\omega^2}{2\pi k^2 \sigma} > 0.18709$  . . . the Jacobian ellipsoids of revolution spheroid. do not exist.

In the case of the Maclaurin spheroids the relation between  $\frac{\omega}{2\pi k^2\sigma}$  and the eccentricity, e, of an axial section is given by the well-known equation<sup>3</sup>

$$\frac{\omega^2}{2\pi k^2 \sigma} = \frac{1}{\lambda^2} \left\{ \frac{(3+\lambda^2)}{\lambda} \tan^{-1} \lambda - 3 \right\} = \phi(\lambda) \tag{1}$$

where

$$\lambda = \frac{e}{\sqrt{1 - e^2}}$$

It follows from these equations that for  $\lambda = 0$  we have

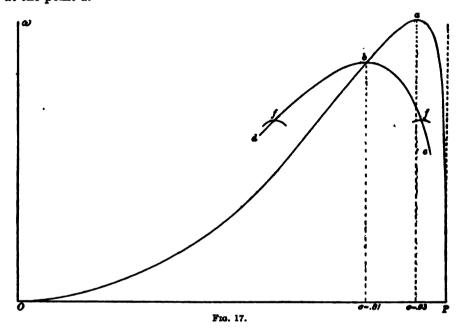
$$\psi(\lambda) = 0 \qquad \frac{\partial \psi(\lambda)}{\partial \lambda} = 0 \qquad e = 0 \qquad \frac{\partial \lambda}{\partial e} = 1 \qquad \frac{\partial \psi}{\partial e} = \frac{\partial \psi}{\partial \lambda} \frac{\partial \lambda}{\partial e} = 0$$

and that for  $\lambda = \infty$  we have

$$\psi(\lambda) = 0$$
  $e = 1$   $\frac{\partial \psi}{\partial e} = \infty$ 

Treatise on Fluxions, Edinburgh, 1742.
 Letter to the French Academy, 1834.
 Tisserand, Mécanique Céleste, 2, Chap. VI.

It is well known that  $\frac{\partial \psi(\lambda)}{\partial \lambda}$  passes through zero but once between  $\lambda = 0$  and  $\lambda = \infty$ . Hence we may represent in figure 17 the facts so far enunciated. As  $\omega$  starts from zero and increases, there is a series of figures of equilibrium starting from O and another from P, the two series coinciding and vanishing at the point a.



We may also indicate the existence of the Jacobian ellipsoids of equilibrium on this figure, without, however, being able to define completely their shape by a single point on a curve. Let us represent the eccentricities of the sections made by planes passing through the axis of rotation and each of the other two axes of the ellipsoid by abscissas in figure 17. The Jacobian ellipsoids branch from the Maclaurin spheroids at b. For a given value of  $\frac{\omega^2}{2\pi k^2 \sigma}$  the corresponding point on the curve bc gives the eccentricity of the section through the longest axis and the axis of rotation, while the corresponding point on bd gives the eccentricity of the section through the remaining axis and the axis of rotation. These two points together com-

However, we shall regard the two series of ellipsoids bc and bd as distinct, the properties indicated by a point on either of them being sufficient, when taken with certain equations of relation not represented on the diagram, completely to define the figure. That is, each curve of the whole diagram will be regarded as carrying with it a certain set of equations which serve to complete the definition of the shape of the figure of equilibrium corresponding to each of its points. Thus, OaP carries with it the equation which says that the eccentricity of every plane section through the axis is  $\epsilon$ .

pletely define the shape of the ellipsoid.

The equations associated with db state that the figure is an ellipsoid, and relate the eccentricity given by the point of this curve with the eccentricity of the other principal section by means of elliptic integrals. From this point of view the figures corresponding to points on the curve bd are quite distinct from those on bc, and it is regarded simply as an interesting fact that they are the same in shape and differ only by their orientation in space. For sufficiently small  $\omega$  there are two figures of this kind. When  $\omega$  increases so that  $\frac{\omega^2}{2\pi k^2 \sigma} = 0.18709$ ... they become identical with each other and with the Maclaurin spheroid and vanish at this point.

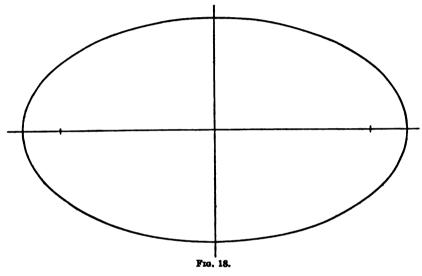


Figure 18 is a scale drawing of an axial section of the Maclaurin spheroid corresponding to the point b of figure 17, and is therefore the figure from which the Jacobian ellipsoids branch. The eccentricity of its axial section is 0.813, or more than twice that of Saturn. In fact, there is no known celestial mass condensed beyond the nebulous state which approaches the oblateness of this theoretical figure of equilibrium.

<sup>&</sup>lt;sup>1</sup> Tisserand, Mécanique Céleste, 2, Chap. VII.

#### III. POINCARÉ'S THEOREMS RESPECTING FORMS OF BIFURCATION AND EXCHANGE OF STABILITIES.

In a memoir 1 remarkable for its powerful methods and important results, Poincaré has proved the existence of an infinite number of other forms of equilibrium. He considered the equations for equilibrium as functions of the number of solutions. For example, for  $\frac{\omega_0^2}{2\pi k^2 \sigma} < 0.22467$  there is a solution on Oa and one on Pa of figure 17. If  $\frac{\omega_0^2}{2\pi k^2 \sigma} < 0.18700$  there is a solution parameter  $\omega$ . For a definite value of  $\omega$ , as  $\omega = \omega_0$ , they have a certain

on Oa and one on Pa of figure 17. If  $\frac{\omega_0}{2\pi k^2 \sigma} < 0.18709$  there are also solutions on bc and bd. If for  $\omega = \omega_1$  two or more solutions unite and do not vanish as  $\omega$  passes through  $\omega_i$ , then the figure of equilibrium corresponding to  $\omega_i$ is a form of bifurcation. If after uniting they vanish, the figure is a limit form. Thus, in figure 17, b belongs to a form of bifurcation, for at this point the Maclaurin spheroids and Jacobian ellipsoids are identical. The point a belongs to limit form, for at this point the two series of Maclaurin spheroids, Oa and Pa, unite and vanish. Likewise the point b belongs to a limit form for the series bd and bc.

Poincaré showed in the work cited that there are no forms of bifurcation corresponding to points on the curve Ob, but that there is an infinite number of them on baP. He proved also that there is an infinite number of them on bc and bd between the point b and the axis  $\omega = 0$ . That is, in addition to the spheroids and ellipsoids of equilibrium an infinite number of other forms exist. The first one on bc is at f, and its deviation from the Jacobian ellipsoid to the first order of small quantities depends upon the third zonal harmonic with respect to the greatest axis of the ellipsoid. It is the pear-shaped figure referred to above. Since it is unsymmetrical with respect to the axis of rotation, there are really two similar figures, differing by 180° in orientation, just as the two series of Jacobian ellipsoids differ by 90° in orientation. There is of course a precisely similar series on bd.

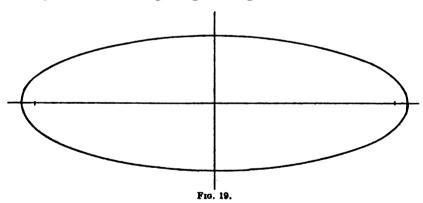
If two real series of figures of equilibrium, A and B, cross, and if before crossing A is stable and B unstable, then after crossing A is unstable and Bhas at least one degree less of instability. Poincaré has also proved an entirely similar theorem in periodic solutions of the problem of three bodies.2

All the spheroids corresponding to points on the curve Ob of figure 17 are completely and secularly stable. At b the spheroids lose their stability but the branching Jacobian ellipsoids are stable. They remain stable until f is reached. It is an interesting question whether the pear-shaped figures are stable or unstable. Poincaré threw the determination of the answer to the question into a form capable of numerical treatment,3 and Darwin has made an elaborate and detailed discussion of it.4 The rigorous answer turns

¹ Sur l'équilibre d'une masse fluide animée d'un mouvement de rotation. <Acta Mathematica, 7, 1885, 259-380.
² Les Méthodes Nouvelles de la Mécanique Céleste, 3, pp. 347-349.
³ Sur la stabilité de l'équilibre des figures pyriformes affectées par une masse fluide en rotation. <Phil. Trans., A, 198 (1902), pp. 333-373.
⁴ The stability of the pear-shaped figure of equilibrium of a rotating mass of liquid. <Phil. Trans., A, 200 (1903), pp. 251-314.

on the numerical value of the sum of an infinite series; and from a computation of its first terms Darwin regards it as certain, though not algebraically proved, that the pear-shaped figure is stable. However, Liapounoff has stated that these figures are unstable. If so, the line of completely stable figures terminates at this point, and as soon as a body has passed beyond it a slight disturbance will cause it to undergo radical changes of form and perhaps break into many fragments. Even if the pear-shaped figures are at first stable, they may become unstable as well as all figures which branch from them long before fission occurs. Indeed, this now seems probable, for Darwin has found,2 in a memoir on the figure and stability of a liquid satellite, that a satellite loses its stability before it can be brought near enough to its primary to coalesce with it.

Consequently if a slightly viscous fluid mass were originally turning slowly and had the form of a stable Maclaurin spheroid of equilibrium, and if in some way greater and greater rates of rotation were gradually impressed upon it without violently disturbing its figure, then we should see the series of changes in its shape described by a point moving along the curve Ob to the point b, then branching on to the line bc of stable forms, again branching at f, if the pear-shaped figures are stable, and continuing along lines of stable figures until they terminate or until fission takes place. At any rate there is no possible chance of fission until the change of shape has passed beyond b, for up to this point there is secular stability and no branching. In fact, we may feel assured that it can not occur until the shape of the mass has passed at least to f. In order that we may see to what a remarkable extent a rotating homogeneous fluid must depart from sphericity before there is a possibility of fission starting, we give in figure 19 the most oblate section



of the ellipsoid belonging to the point f. Darwin has shown that its eccentricity is e = 0.9386. The eccentricity of the other principal section through the axis of rotation is e' = 0.6021, and the eccentricity of the principal section perpendicular to the axis of rotation is e'' = 0.9018.

<sup>&</sup>lt;sup>1</sup> Acad. Imp. des Sci. de St. Pétersbourg, 17, No. 3 (1905).

<sup>2</sup> Phil. Trans., A, 206 (1906), pp. 161–248.

<sup>3</sup> On the pear-shaped figure of equilibrium of a rotating mass of liquid. < Phil. Trans., A, 198 (1902), pp. 301–331.

The points of bifurcation and conditions of stability or instability depend only upon the shape of the figures, while the shapes of the figures in the various series depend only upon the values of  $\frac{\omega^2}{2\pi k^2 \sigma}$ . Consequently if a rotating homogeneous fluid body contracts in such a way as to remain always homogeneous, its shape and condition as to stability are determined by this function throughout the whole series of changes.

#### IV. FIGURES OF EQUILIBRIUM OF ROTATING HETEROGENEOUS FLUIDS.

We now enter a field beset with formidable difficulties and in which there are but few positive results. We shall consider masses which are possessed of slow rotation, which grow continually denser toward their centers, and which are approximately spherical in form. To simplify the problem we may suppose first that we have under consideration a body composed of a number of incompressible fluids of different densities, arranged in order of increasing density from the surface to the center. This hypothesis more nearly agrees with the conditions found in nature than that of homogeneity does, and the results obtained under it may be taken as throwing light on the actual problems.

Clairaut has shown that such a body as we are considering will always be less oblate than it would if its mass were uniformly distributed throughout its volume. This is easy to see in considering the limiting case of a dense nucleus surrounded by a homogeneous atmosphere of vanishing mass. That this result may be legitimately applied to the celestial bodies is proved by the fact that the earth, Jupiter, and Saturn are all less oblate than they would be if they were homogeneous and rotating at their respective rates. It is an interesting and important fact that the differences in oblateness of these planets and the corresponding homogeneous figures of equilibrium are greater the smaller the mean density. That is, if a low mean density means the mass is largely gaseous and compressible, we may conclude that the more a body is condensed toward its center the less oblate it will be for a given rate of rotation. The facts for the earth, Jupiter, and Saturn are given in the following table, where s has been computed from equation (1).

	Recentricity of meridian section if homogeneous.	Observed eccentricity of meridian section.
Earth	.096	.083
Jupiter.	.461	.347
Saturn	.607	.409

Consider still the case of a heterogeneous incompressible fluid mass with greatest density at its center. Suppose the density is given by an equation of the form  $\sigma = \sigma_0 + \epsilon \sigma_1$ 

where  $\sigma_0$  is the mean density of the whole mass, and where  $\sigma_1$  is always finite and may be a continuous function of  $\epsilon$ . For  $\epsilon=0$  certain series of figures of equilibrium are represented in figure 17. Let us suppose there is a third axis in the figure perpendicular to the ε and ω-axes. We shall mark off values of e along this axis.

Let the conditions for a figure of equilibrium be

$$F_i(x_1, \ldots, x_n, \omega, \varepsilon) = 0, \ i = 1, \ldots, n$$
 (3)

<sup>&</sup>lt;sup>1</sup> See Tisserand's Mécanique Céleste, 2, Chap. XIII.

For  $\epsilon = 0$  and  $\frac{\omega}{2\pi k^2 \sigma_{\bullet}}$ -<0.22467 . . . certain solutions are represented by points on the curves of figure 17. Suppose for  $\omega = \omega_0$  the solution  $x_i = x_i^{(0)}$ is not a multiple solution. The F, depend upon the gravitational potential and the rotational energy, and are continuous functions of c. Consequently the roots of (3) vary continuously with e, and we may represent their solution by a point in figure 17 in the plane  $\epsilon = \epsilon$ , where as before, each linear series with respect to a parameter, as  $\frac{\omega^2}{2\pi k^2\sigma_0}$  or  $\epsilon$ , carries with it a set of relations which completely defines the shape of the figure of equilibrium. If  $\omega = \omega_0$  and  $\epsilon = 0$  belong to a multiple solution of (3) there is an  $\omega$  near  $\omega_0$  such that for  $\epsilon = \epsilon$  equations (3) have also a multiple solution. By this process the curves of figure 17 become surfaces to every point of which belongs a figure of equilibrium. If in this figure  $\epsilon$  is set equal to a small constant a new set of curves will be obtained in a general way similar to the old, and possessing maxima and points of bifurcation. In general the greater e the greater will be their deviation from the forms of the curves in figure 17.

Now consider the question of stability. The necessary and sufficient condition for complete and secular stability of the figure of equilibrium is that the total energy shall be a minimum for all variations preserving constant moment of momentum.1 All the quantities involved in these conditions are continuous functions of  $\epsilon$ . Consequently, starting from an ordinary point in figure 17 whose corresponding figure of equilibrium has any properties of stability, it is found that the figure obtained by varying e through a sufficiently small range will have the same properties of stability. Consider the curves obtained by giving  $\epsilon$  a constant value. At certain places the figures of equilibrium will change the character of their stability; but as in the case of  $\epsilon = 0$ , treated by Poincaré, wherever the stability changes a new series of figures branches out. Since the curves for  $\epsilon = \epsilon$  are in the analytic sense the continuation of those for  $\epsilon = 0$ , the figures of equilibrium for  $\varepsilon = \varepsilon$  go through a series of changes of stability entirely analogous to the changes in the figures for  $\epsilon = 0$ . Of course, it is possible that two curves,  $C_0'$  and  $C_0''$ , might cross a curve  $C_0$  at a single point for  $\epsilon=0$ , and that the corresponding curves,  $C_{\epsilon}'$  and  $C_{\epsilon}''$ , might cross the curve  $C_{\epsilon}$  in two distinct points, or the opposite. For example, there might be such a definition of  $\sigma_1$ that, for a certain value of  $\epsilon$ , the point corresponding to f of figure 17 would fall on the point corresponding to b. However, in the present connection such exceptional cases are trivial. The point of interest is that for  $\epsilon = \epsilon > 0$ there is a line of stable figures of equilibrium corresponding to those for which this parameter is zero.

In general, for  $\epsilon > 0$ , the point of bifurcation corresponding to b, figure 17, will not appear for the same value of  $\omega$  as that belonging to b. We may represent these two values of  $\omega$  by  $\omega_{\epsilon}$  and  $\omega_{0}$  respectively. The question of interest in the present connection is which is the greater; or, in other terms, whether with increasing rotation instability occurs first in the heterogeneous or in the homogeneous body. We shall not attempt a positive

<sup>&</sup>lt;sup>1</sup> Thomson and Tait's Natural Phil., Part II, 778, (j) and (k).

answer to this question, but in view of the fact that for a given rotation and mean density the homogeneous body is more oblate than the heterogeneous body, we are justified in concluding that probably instability first appears in the figures of equilibrium for  $\varepsilon = 0$ .

Now consider the case of a heterogeneous compressible rotating fluid. The preceding remarks pertaining to the existence of the figures of equilibrium still hold, though all the explicit defining equations are immensely more complicated. But the question of stability has a new element in it. As Jeans has shown in an important memoir, gravitation itself becomes a source of instability. It is easy to see that if for any reason there is a local condensation in a compressible fluid, gravitation will tend to augment this condensation. On the other hand, the elastic forces called into play tend to destroy the condensation. The two kinds of forces are in conflict, and the state of stability depends upon which will predominate when the equilibrium is disturbed. Jeans showed that an infinitely extended nebula, of density such that it possesses the properties of gases, is in unstable equilibrium independently of its mean temperature and density. That is, in this case it is possible to introduce such local variations in density that the decrease in gravitational potential energy shall more than balance the increase in the potential energy of the elastic forces.

There are as yet no quantitative results by means of which we may measure the importance of this factor of instability. It is true that Jeans and Love have proved the stability of the earth under certain assumptions, but in view of its present existence, notwithstanding the many vicissitudes which it has survived, this result may be taken as reflecting favorably upon the method employed in obtaining it, rather than assuring us of the permanency of our planet. In the absence of positive quantitative results we are able to make only more or less probable hypotheses as to the importance of this factor.

There are seen to be two opposing factors entering into the question of stability of heterogeneous compressible masses. As compared with homogeneous incompressible masses, the central condensation tends strongly toward sphericity, as is shown both by theory and by the observed shape of the sun and planets, and therefore presumably toward stability. But the compressibility tends toward instability for local deformations and alterations in density. We shall assume as appearing reasonable that in bodies having strong central condensations and continuous changes in density these two opposing factors approximately balance. To the extent to which this assumption is justified, we may draw conclusions in regard to the actual celestial bodies from what is known regarding the forms and stabilities of homogeneous fluids. For the purposes of additional safety in this procedure we shall keep far from the conditions of possible disruption in the applications which follow.

The stability of a spherical nebula. < Phil. Trans., A, 199 (1902), pp. 1-53.</li>
 On the vibrations and stability of a gravitating planet. < Phil. Trans., A, 201 (1903), pp. 157-184.</li>
 The gravitational stability of the earth. < Phil. Trans., A, 207 (1908), pp. 171-241.</li>

### V. THE EQUATIONS OF EQUILIBRIUM FOR CONSTANT MOMENT OF MOMENTUM.

Equation (1) is the relation connecting the shape of the Maclaurin spheroid, its density, and its rate of rotation. Let m represent its mass, a its polar radius, and M its moment of momentum. Then we have

$$m = \frac{4}{3}\pi a^3 (1 + \lambda^2)\sigma \tag{4}$$

$$M = \frac{2}{3}ma^2(1+\lambda^2)\omega \tag{5}$$

Eliminating  $\omega$  and a between equations (1), (4), and (5), we have

$$\frac{25(\frac{4}{3}\pi)^{\frac{1}{3}}M^{2}}{6k^{2}m^{\frac{1}{3}}}\sigma^{\frac{1}{3}} = \frac{(1+\lambda^{2})^{\frac{3}{3}}}{\lambda^{2}} \left\{ \frac{(3+\lambda^{2})}{\lambda} \tan^{-1}\lambda - 3 \right\}$$
 (6)

For a homogeneous body of given mass and moment of momentum, this is a relation between the density and oblateness which must always be satisfied so long as the figure is a spheroid. It is easily verified that  $\frac{\partial \sigma^t}{\partial \lambda^2}$  is positive for all real values of  $\lambda$ , from which it follows that when the left member of the equation is given there is but a single real solution for  $\lambda^2$ .

The Jacobian ellipsoids are defined by the equations<sup>1</sup>

$$o = \int_{0}^{1} \frac{\zeta^{2}(1-\zeta^{2})(1-\lambda^{2}\lambda'^{2}\zeta^{2})d\zeta}{(1+\lambda^{2}\zeta^{2})^{\frac{3}{2}}(1+\lambda'^{2}\zeta^{2})^{\frac{3}{2}}}$$
(7)

$$\frac{\omega^{2}}{2\pi k^{2}\sigma} = 2\sqrt{1+\lambda^{2}} \sqrt{1+\lambda^{\prime 2}} \int_{0}^{1} \frac{\zeta^{2}(1-\zeta^{2})d\zeta}{(1+\lambda^{2}\zeta^{2})^{\frac{3}{2}} (1+\lambda^{\prime 2}\zeta^{2})^{\frac{3}{2}}}$$
(8)

where the axes of the ellipsoid are a, b, and c, and

$$b^2 = a^2(1 + \lambda^2)$$
  $c^2 = a^2(1 + \lambda'^2)$ 

Equation (7) defines the relation between  $\lambda$  and  $\lambda'$  which must be satisfied by these figures of equilibrium, and equation (8) expresses  $\frac{\omega^2}{\sigma}$  in terms of  $\lambda^2$  and  $\lambda'^2$ .

The equations corresponding to (4) and (5) are in this case

$$m = \frac{4}{8}\pi a^3 \sqrt{1 + \lambda^2} \sqrt{1 + \lambda'^2} \sigma \qquad M = \frac{ma^2}{5} (2 + \lambda^2 + \lambda'^2) \omega \qquad (9)$$

By means of these relations, equation (8) reduces to

$$\frac{25(\frac{4}{8}\pi)^{\frac{1}{8}}M^{2}}{3k^{2}m^{\frac{1}{4}}}\sigma^{\frac{1}{8}} = \frac{(2+\lambda^{2}+\lambda^{\prime2})}{(1+\lambda^{2})^{\frac{1}{8}}(1+\lambda^{\prime2})^{\frac{1}{8}}}\int_{0}^{1} \frac{\zeta^{2}(1-\zeta^{2})d\zeta}{(1+\lambda^{2}\zeta^{2})^{\frac{1}{8}}(1+\lambda^{\prime2}\zeta^{2})^{\frac{1}{8}}}$$
(10)

Now we may write (7) and (10) respectively

$$\theta(\lambda, \lambda') = 0 \qquad \qquad \varphi(\lambda, \lambda') = K\sigma^{\frac{1}{2}} \tag{11}$$

<sup>&</sup>lt;sup>1</sup> Tisserand's Mécanique Céleste, 2, Chap. VII.

where K is a constant depending upon m and M. From these equations we have

$$\frac{\partial \theta}{\partial \lambda} \delta \lambda + \frac{\partial \theta}{\partial \lambda'} \delta \lambda' = 0$$
$$\frac{\partial \varphi}{\partial \lambda} \delta \lambda + \frac{\partial \varphi}{\partial \lambda'} \delta \lambda' = \frac{1}{8} \frac{K}{\sigma^{\frac{3}{4}}} \delta \sigma$$

Then we find

$$\delta \lambda = -\frac{1}{3 A} \frac{K}{\sigma^{\frac{1}{4}}} \frac{\partial \theta}{\partial \lambda'} \delta \sigma \qquad \qquad \delta \lambda' = +\frac{1}{3 A} \frac{K}{\sigma^{\frac{1}{4}}} \frac{\partial \theta}{\partial \lambda} \delta \sigma \qquad (12)$$

where

$$\mathbf{\Delta} = \begin{vmatrix} \frac{\partial \theta}{\partial \lambda} & , & \frac{\partial \theta}{\partial \lambda'} \\ \frac{\partial \varphi}{\partial \lambda} & , & \frac{\partial \varphi}{\partial \lambda'} \end{vmatrix}$$

Since  $\lambda$  and  $\lambda'$  enter  $\theta$  and  $\varphi$  symmetrically, it follows that when the ellipsoid branches from the Maclaurin spheroid, i.e., when  $\lambda = \lambda'$ , we have  $\frac{\partial \theta}{\partial \lambda} = \frac{\partial \theta}{\partial \lambda'}$ . Hence as the ellipsoid branches from the spheroid because of increasing density, the eccentricity of one principal axial section increases while that of the other decreases. This continues indefinitely unless either  $\frac{\partial \theta}{\partial \lambda}$  or  $\frac{\partial \theta}{\partial \lambda'}$  vanishes, which is extremely unlikely. This means the figure tends to become cigar-shaped. At a certain elongation (see figure 19) the so-called pear-shaped figure branches. Certainly in homogeneous masses there can be no fission before this elongation, with its corresponding density, is attained.

#### VI. APPLICATIONS TO THE SOLAR SYSTEM.

In applying the formulas above to the solar system we must remember that they are strictly valid only when the masses are homogeneous. Now the sun and planets are certainly not homogeneous, but we have seen reasons for believing that nevertheless the formulas will give results which are not remote from the truth. But, because of this uncertainty, in the applications which follow we shall not attempt to draw conclusions except where the margin of safety is extremely great.

Let us consider first the sun. We shall find its density for various degrees of oblateness, and its oblateness for a certain very high density.¹ Referring to (6) we see that the greater the moment of momentum of a body the less dense it will be for a given oblateness, and the more oblate it will be for a given density. Consequently we shall be favoring the conclusion that the sun will eventually suffer fission if we use too large a value of M. The moment of momentum is most easily computed if we suppose the sun is homogeneous, and the result obtained in this way will certainly be in excess of the true value.

Using the mean solar day, the mean distance from the earth to the sun, and the mass of the sun, as the units of time, distance, and mass respectively, we find that the density of water is

$$\sigma_{\text{water}} = 1,567,500.$$

Taking the sun's density as 1.41 on the water standard, its period of rotation as 25.3 days, and its radius as 433,000 miles, we find for its moment of momentum

 $M_{\rm sun}=\frac{216}{10^8}$ 

Now we may apply equation (6) to find how dense the sun will be before the Jacobian ellipsoids branch off. It is hardly possible that the sun could suffer fission before this point is reached, the shape of the spheroid being given in figure 19. The computation shows that when the sun shall have reached this degree of oblateness its density will be

$$\sigma\!=\!307\times10^{11}$$
 on the water standard.

This density corresponds to an equatorial radius of the sun of 11 miles. Since this density is millions of times greater than it is supposed matter ever attains under any circumstances, we must conclude that the oblateness of the sun can never approach that for which the Jacobian figures of equilibrium branch. Or, in brief, the sun can never contract so much that its rotation will threaten it with disruption.

Notwithstanding the extreme character of these figures, one might still be so ultra-skeptical as to doubt the conclusion, since it is based on the computation of the point of bifurcation for homogeneous masses. However that may be, we must admit that the sun will be stable until its oblateness reaches that of Saturn at present. We have seen that the eccentricity of a

<sup>&</sup>lt;sup>1</sup> Strictly speaking the computations are made for homogeneous bodies of the same mass and having the same moment of momentum, but no confusion will result from this mode of expression.

meridian section of a homogeneous fluid having the mass and the mean density of Saturn, and rotating in its period, would be 0.607. Since the constitution of the sun is in a general way like that of Saturn, it will have the oblateness of Saturn about when the section of the corresponding homogeneous mass has this eccentricity. Making the computation from equation (6) we find that the sun will not become so oblate as Saturn is now until its mean density becomes  $148 \times 10^{10}$  on the water standard. This corresponds to a radius of 37.3 miles. If we may regard this as an impossibly large density we may conclude that the sun will never be so oblate as Saturn is now, and that its stability will always be greater than that of Saturn at present.

Apparently the chances that Saturn will separate into two parts because of shrinking and rapid rotation are greater than that any other member of the solar system will ever suffer fission. To examine the probabilities we shall apply equations (4), (5), and (6) to Saturn. Taking the density, mass, and period of rotation as 0.72,  $\frac{1}{8502}$ , and 10.25 hours respectively, and computing the moment of momentum under the hypothesis that Saturn is now a homogeneous sphere, in order to give the theory that fission is possible all the benefits of the approximations, we find that when Saturn shall have an oblateness equal to that of the spheroids from which the Jacobian ellipsoids branch, its density will be 21 times that of water, its axial diameter 16,500 miles, its equatorial diameter 28,400 miles, and its period of rotation 1 hr. 24 m. The high mean density demanded seems to be fatal to the theory of fission in this case.

In order to see how great changes in the density, dimensions, and period the body will undergo by the time it reaches the state where the pear-shaped figures branch, we may apply equations (7), (9), and (10) to Saturn. Darwin has made the computations from equations equivalent to (7) and (8), and has found that for this point

$$\lambda = 0.7544$$
  $\lambda' = 2.7206$   $\frac{\omega^2}{2\pi k^2 \sigma} = 0.1420$ 

Then equations (9) show that at this stage the mean density of Saturn must be 93 on the water standard, its polar diameter 9,400 miles, its longest diameter 27,000 miles, and its period of rotation 46 minutes. That is, the mass is about four and one-half times as dense when the pear-shaped figures branch as when the Jacobian ellipsoids branch. While the computation was applied to Saturn, it follows from equations (6) and (10) that this same ratio for the densities at these critical forms is true, whatever the mass and moment of momentum of the body under consideration.

The density which the earth will attain before it will reach one of the critical forms is so great that the computation is without interest. But we may examine the hypothesis that the earth and moon were originally joined in one mass whose rapid rotation produced instability, and that resulting fission gave rise to two bodies having great stability. It is to be observed in the first place that the moment of momentum of the earth-moon system has remained constant except for influences exterior to itself. There is none

<sup>&</sup>lt;sup>1</sup> Phil. Trans., A, 198 (1902), p. 326.

readily assignable which could have increased it. Among those which may have decreased it apparently the solar tidal friction is the only one which can have produced sensible results.

The effect of the moon's tides in the earth has been to transfer moment of momentum from the earth to the moon. According to the results given in the preceding paper on tidal evolution, section XIV, the maximum moment of momentum the earth-moon system could have had, including all that the sun could have taken from it, is that belonging to the system moving as a rigid mass with a period of 4.8 hrs. Let P represent this common period. Then, neglecting the inclinations of the planes of the equators of the earth and moon to the plane of their orbit and the possible eccentricity of their orbit, factors which reduce the moment of momentum, we have by equation (6), loc. cit.,

$$M = \frac{m_1 m_2 k^{\frac{1}{2}} P^{\frac{1}{2}}}{(2\pi)^{\frac{1}{2}} (m_1 + m_2)^{\frac{1}{2}}} + \frac{2\pi c_1 m_1 a_1^2}{P} + \frac{2\pi c_2 m_2 a_2^2}{P}$$
(13)

The quantities  $c_1$  and  $c_2$  depend upon the distribution of mass throughout  $m_1$  and  $m_2$ ,  $m_1$  representing the earth, and  $m_2$  the moon. If the masses are homogeneous  $c_1=c_2=0.4$ . If they obey the Laplacian law of density  $c_1=c_2=0.336$ . If the distribution of mass is such that the densities increase from the surfaces to the centers of these bodies, the values of  $c_1$  and  $c_2$  are less than 0.4. We shall certainly get too large a value for M by putting  $c_1=c_2=0.4$ . Adopting these values we find that for the earth-moon system, in the units of this paper,  $M=8\times10^{-14}$ .

Since large moment of momentum tends to instability we shall favor the theory of fission if we add 25 per cent to this number, supposing that perhaps this amount may have been lost through meteoric or other friction. Then, using  $M=10^{-18}$  and  $m=3\times 10^{-6}$ , equation (6) gives for this united earth-moon mass at the time when the Jacobian ellipsoid branched a mean density 215 times that of water. We find similarly that this hypothetical earth-moon mass could not become even so oblate as Saturn is now until its density had become 10.4 times that of water. Since the present density of the earth is only 5.53, this means that if the hypotheses upon which this computation was made are valid, the earth-moon system can not have arisen from the fission of a parent mass under the influence of rapid rotation.

In the preceding paper, starting with the earth-moon system as it now exists and following backward in time the effects of tidal friction, it was not possible to get the earth and moon in close enough proximity to make the fission theory seem possible. Now, starting with the supposed initial system with the critical factor, the moment of momentum, determined from observations, we do not find the figure approaching an unstable form until the density is more than 40 times the present density of the earth.

#### VII. APPLICATION TO BINARY STARS.

Direct telescopic observations prove the existence of very many binary stars. According to Hussey and Aitken about one star in 18 of those brighter than the ninth magnitude is a visual double. There are many stars whose spectra periodically consist of double lines. This phenomenon is taken as indicating that these stars are binary systems, made up of two approximately equal components, whose orbital planes pass nearly through the earth. There are many more stars whose spectral lines periodically shift. This is interpreted as meaning that these systems are binaries in each of which one component is relatively non-luminous. There are many variable stars whose light curves are explained by supposing they are eclipsing binary systems. Unless the interpretations of these phenomena are very much in error a considerable fraction of all the stars are binaries. Granting that the interpretations are correct, the evolution of binary systems is a standard celestial process. We are raising the question here whether these binaries may have originated from parent masses by fission without external disturbing factors, and if so at what stage of condensation.

Before considering the question of the fission of single masses into binary systems, we shall write down some of the implications of the interpretations of the spectra of spectroscopic binaries, particularly as regards limits on their masses and densities.

Consider first the case where both spectra are visible. Let i be the complement of the inclination of the plane of the orbit to the line of sight. Suppose the orbit is circular. Let v be the maximum observed radial velocity,  $m_1$  and  $m_2$  the two masses, P the period of revolution, and a the major semi-axis of the orbit.

Then we have

$$\frac{Pv}{\cos i} = 2\pi a \qquad P = \frac{2\pi a^{\frac{3}{2}}}{k\sqrt{m_1 + m_2}} \qquad m_1 + m_2 = \frac{Pv^{\frac{3}{2}}}{2\pi k^2 \cos^3 i} \qquad (14)$$

Since i can not be determined in a star which is not also a visual binary we have, reducing the units so that when v is expressed in kilometers per second and P in mean solar days, the sum  $m_1 + m_2$  expressed in terms of the sun's mass by the relation

 $m_1 + m_3 \ge \frac{178}{10^8} Pv^8 \tag{15}$ 

Suppose the spectrum of only one star,  $m_1$ , is visible, and let  $v_1$  be its maximum observed radial velocity with respect to that of the center of gravity of the system. Let  $r_1$  be the radius of its orbit, assumed to be circular, around the center of gravity of the system. Then we have

$$\frac{Pv_1}{\cos i} = 2\pi r_1 \qquad m_1 r_1 = m_2 r_2 \qquad a = r_1 + r_2 \qquad P = \frac{2\pi r_1^{\frac{3}{2}} (m_1 + m_2)}{k m_2^{\frac{3}{2}}}$$
whence
$$m_2 = \frac{Pv_1^{\frac{3}{2}} \left(1 + \frac{m_1}{m_2}\right)^2}{2\pi k^2 \cos^3 i} \qquad (16)$$

In this case the lower limit of the mass of the system can not be computed except an assumption be made regarding the relation between  $m_1$  and  $m_2$ . Suppose  $\frac{m_1}{m_2} = \mu$ . Then equation (16) gives

$$m_1 + m_2 = (1 + \mu) m_2 \ge \frac{P v_1^3 (1 + \mu)^3}{2\pi k^2}$$
 (17)

When P is expressed in mean solar days, and  $v_1$  in kilometers per second, we

 $m_1 + m_2 \ge \frac{178}{10^8} P v_1^8 (1 + \mu)^8$ 

where  $m_1 + m_2$  is expressed in terms of the sun's mass. If it were true that the more massive star always gives the observed spectrum we should have  $\mu > 1$  and

 $m_1 + m_2 > \frac{1424}{108} Pv_1^3$ (19)

Let  $a_1$  and  $a_2$  represent the radii of  $m_1$  and  $m_2$  respectively. Let the distance between their surfaces be represented by  $\kappa a$ . Then  $0 \le \kappa < 1$  and we have

$$a_1 + a_2 = a(1 - \kappa) \qquad P = \frac{2\pi (a_1 + a_2)^{\frac{1}{2}}}{k(1 - \kappa)^{\frac{1}{2}} \sqrt{m_1 + m_2}}$$
 (20)

Suppose the two bodies have the same density  $\sigma$ . Then we have from  $m_1 = \frac{4}{3}\pi\sigma a_1^3$ ,  $m_2 = \frac{4}{3}\pi\sigma a_2^3$  and equation (20), putting  $\frac{m_1}{m_2} = \mu$  as before  $\sigma = \frac{3\pi}{k^2 P^2} \frac{(1+\mu^{\frac{1}{2}})^3}{(1-\kappa)^3 (1+\mu)}$  (21)

$$\sigma = \frac{3\pi}{k^2 P^2} \frac{(1+\mu^b)^3}{(1-\kappa)^3 (1+\mu)} \tag{21}$$

The ratio  $\mu$  may vary from zero to infinity, and  $\kappa$  from 0 to 1. From the derivative

$$\frac{\partial \sigma}{\partial \mu} = \frac{3\pi}{k^2 P^2 (1-\kappa)^3} \frac{(1+\mu^{\frac{1}{3}})^2 (1-\mu^{\frac{3}{3}})}{\mu^{\frac{3}{3}} (1+\mu)^2}$$

it follows that, for fixed values of P and  $\kappa$ ,  $\sigma$  constantly increases while  $\mu$ varies from 0 to 1, and then constantly decreases while  $\mu$  varies from 1 to  $\infty$ . Therefore, since (21) is a reciprocal equation in  $\mu$ , we have

$$\frac{12\pi}{k^2(1-\kappa)^3 P^2} \ge \sigma \ge \frac{3\pi}{k^2(1-\kappa)^3 P^2}$$
 (22)

Or, changing the units so that  $\sigma$  will be expressed in terms of the density of water when P is expressed in mean solar days, we have

$$\frac{8}{100 (1-\kappa)^3 P^2} \ge \sigma \ge \frac{2}{100 (1-\kappa)^3 P^2}$$
 (23)

The smaller  $\kappa$  the smaller the limits for  $\sigma$ . When the bodies are in contact, and the period 4.57 hours, that of  $\beta$  Cephei, we find

$$\mathbf{2.2} \! \ge \! \sigma \! \ge \! 0.5$$

<sup>&</sup>lt;sup>1</sup> The Period of  $\beta$  Cephei, by E. B. Frost, Astrophysical Jour., 24 (1906), pp. 259–262.

If they are separated so that their surfaces are at a distance from each other equal to one-half the sum of their radii, i.e., if  $\kappa = \frac{1}{3}$ , equation (23)  $7.4 \ge \sigma \ge 1.8$ 

According to Darwin's results, loc. cit., p. 232, this is about the minimum distance at which homogeneous masses could revolve in stable equilibrium. If they were separated farther the already high limits on the density would be still greater. It follows that we must conclude either that these very short period binaries and eclipsing variables are very dense, or that heterogeneous masses are more stable than homogeneous ones.

Now let us return to the question of fission of binary stars. Denoting the periods of rotation of  $m_1$  and  $m_2$  by  $D_1$  and  $D_2$  respectively, we have for the total moment of momentum of the system 1

$$M = \frac{m_1 m_2 k^{\frac{1}{2}} P^{\frac{1}{2}}}{(2\pi)^{\frac{1}{2}} (m_1 + m_2)^{\frac{1}{2}}} + \frac{2\pi c_1 m_1 a_1^2}{D_1} + \frac{2\pi c_2 m_2 a_2^2}{D_2}$$
(24)

The signs of the second and third terms in this equation are determined under the hypothesis that both bodies rotate in the direction in which they revolve. But this is a necessary consequence of the fission theory, and therefore an allowable assumption in testing it.

If  $P > D_1$  and if  $P > D_2$  then the mutual tides of the two bodies tend to bring P,  $D_1$ , and  $D_2$  eventually to the same value. In the case of widely separated visual binaries the fission theory implies that the tidal evolution has proceeded far, and that  $D_1$  and  $D_2$  are closely approaching an equality with P. If these conditions are satisfied and if  $m_1$  and  $m_2$  are approximately equal, we see from (24) that the inequality

$$M > \frac{m_1 m_2 k^{\frac{1}{2}} P^{\frac{1}{2}}}{(2\pi)^{\frac{1}{2}} (m_1 + m_2)^{\frac{1}{2}}}$$
 (25)

is nearly an equality. For example, in the case of a Centauri, assuming that each component has the dimensions of the sun and that  $D_1 = D_2 = P$  approximately, the ratio of the first term to the sum of the other two is roughly 10,000 to 1. In general, the greater P and the more nearly equal  $m_1$  and  $m_2$ , the more nearly the inequality (25) approaches an equality, and the opposite.

Let us suppose the two stars were originally in one spheroidal mass  $m = m_1 + m_2$ . Then equation (6) gives the relation between its density and oblateness, which reduces by means of (25) to

$$\frac{25m_1^2m_2^2k^{\frac{3}{2}}P^{\frac{3}{2}}}{6(3\pi)^{\frac{1}{2}}(m_1+m_2)^4}\sigma^{\frac{1}{2}} < \frac{(1+\lambda^2)^{\frac{3}{2}}}{\lambda^2} \left\{ \frac{(3+\lambda^2)}{\lambda} \tan^{-1}\lambda - 3 \right\}$$
 (26)

Now let  $\frac{m_1}{m_2} = \mu$ ; then equation (26) gives

$$\sigma^{\frac{1}{2}} < \frac{6(3\pi)^{\frac{1}{6}}(1+\mu)^{4}}{25k^{\frac{6}{2}}P^{\frac{6}{6}}} \frac{(1+\lambda^{2})^{\frac{6}{6}}}{\lambda^{2}} \left\{ \frac{(3+\lambda^{2})}{\lambda} \tan^{-1}\lambda - 3 \right\}$$
 (27)

Letting 
$$f(\mu) = \frac{(1+\mu)^4}{\mu^2}$$
 we find for  $\mu = 1$  that  $\frac{\partial f}{\partial \mu} = 0$ ,  $\frac{\partial^2 f}{\partial \mu^2} > 0$  and that  $\frac{\partial f}{\partial \mu}$ 

vanishes for no other value of  $\mu$ . Consequently the right member of (27) has a single minimum at  $\mu=1$ . But for other values of  $\mu$  the inequality of (27) differs more from an equality, and hence we are not certain that  $\mu=1$  gives the least value of  $\sigma$  for a given P and  $\lambda$ . But in many stars  $\mu$  is undoubtedly near enough unity to make equation (27) useful.

We shall suppose  $\mu=1$  and compute  $\sigma$  for the value of  $\lambda$  for which apparently there is first any danger of fission. If we suppose that this first occurs for that value of  $\lambda$  for which the Jacobian ellipsoids branch, that is for  $\lambda=1.395\ldots$ , we find, taking the units so that  $\sigma$  will be expressed in terms of the density of water when P is expressed in terms of mean solar days.

 $\sigma < \frac{0.016}{P^2} \tag{28}$ 

Or, if the fission occurred when the pear-shaped figures branched from the Jacobian ellipsoid, we find similarly

$$\sigma < \frac{0.071}{P^2} \tag{29}$$

Consequently, this discussion leads to the conclusion that in all binary systems in which the two masses are approximately equal, and in which the periods are at least several years, as they are in the visual pairs, the fission must have occurred, if at all, while the parent mass was yet in the nebulous state. The data regarding binary systems as a class are so meager that probably no stronger conclusion than this can be drawn from this line of argument.

There is, of course, no a priori objection to the theory that binaries as a class have originated by fission in the nebulous state. But there are at least two rather distinct hypotheses as to how and why such fission may have taken place. The first is that in the origin of a nebulous mass the factors which have determined its initial condition may have brought it into existence with at least two nuclei of condensation whose magnitude and density were sufficient to have led to a binary, even though the moment of momentum may have been so low that, if the mass had been spheroidal with the same mean density, it would have been a stable figure. Fission in this type of masses is not under consideration here. The second is that the mass in its earliest nebulous stage was in an approximately spheroidal form, densest at its center with density decreasing outward through approximately spheroidal layers, and that as a consequence of its high moment of momentum it lost its stability and divided into two masses. This is the type of fission under consideration here.

Suppose a nebula of this latter type suffers fission. At the time of fission all parts are rotating at the same angular rate, and one of the two parts must have a mean density less than, or at the most equal to, the mean density of the original mass. Consequently one of the two fragments because of its lower density and equal rotation, must have at least as great a tendency to fission as that which led to the division of the initial mass, unless either its form is one of greater stability, or the tidal forces of the other member of the pair tend to keep it from breaking up. If, as seems probable, the approximate spheroid is the most stable figure of equilibrium, and if the mass

under consideration has suffered fission by evolution along this line of figures, as is assumed, then the former alternative is eliminated. It does not seem that the tidal factor can tend toward stability. This intuition is strongly supported by the results obtained by Darwin, loc. cit., attacking the problem from the other end, viz., that it is not possible to bring two homogeneous fluid masses near enough to touch without their being certainly in unstable equilibrium.

We observe next that the binary stars are now actual stars of considerable density. Consequently if they have originated from the fission of nebulas they have undergone enormous contraction. The contraction implies increased rotation which would increase the already dangerous tendency for at least one part to suffer further fission. Tidal friction would offset this tendency by decreasing the rotations, but considering all the factors involved, it is seen that if a fluid mass ever gets to the state where fission occurs, there is at least great danger of its breaking into many pieces.

Consequently we are led to believe that if binaries and multiple stars of several members have developed from nebulas, the nebulas must originally have had well-defined nuclei. The photographs of many nebulas support this conclusion. But we observe that if we are forced to this position we do not explain anything—we only push by an assumption the problem of explaining the binary systems a little farther back into

the unknown.

# VIII. SUMMARY.

The problem under consideration is that of the fission of celestial bodies because of rapid rotation when they are not disturbed by important external forces. The attack is made through well-known results concerning the figures of equilibrium and conditions as to stability of rotating homogeneous incompressible fluids. It is recalled that for slow rotation a nearly spherical oblate spheroid is a stable form of equilibrium; that for greater rates of rotation the corresponding figure is more oblate; that when the eccentricity of a meridian section becomes 0.813 the figure loses its stability and at this point a stable line of three axis ellipsoids branches; that when the longest axis of the ellipsoid becomes about three times the axis of rotation a new series, known as the pear-shaped figures (or better, perhaps, the cucumbershaped figures) branches, and that before this point is reached there is no possibility of fission. We are almost entirely ignorant as to what may happen after this point is passed, and it must be remembered that it has not been proved that in any case fission into two stable bodies is possible.

The celestial bodies differ from those just considered in two important respects. In the first place their densities increase toward their centers. For a given rate of rotation and mean density this central condensation makes them more nearly spherical, as is shown both by theory and by comparison of the observed figures of the planets with the computed forms of corresponding homogeneous masses. In the case of Saturn, for example, the eccentricity computed on the hypothesis of homogeneity is 0.607 while the observed value is only 0.409. It seems certain that this central condensation tends toward stability. The second important difference between the ideal homogeneous incompressible fluids and the celestial bodies is that the latter are compressible. This latter factor, at least under certain circumstances, tends toward instability.

The opposing quantitative effects of central density and compressibility undoubtedly differ greatly in different masses and can not be easily determined in any case. However, if we may assume that they approximately offset each other, we may reach some conclusion respecting the possibility of the fission of the actual celestial bodies by discussing the corresponding homogeneous incompressible body. This is the assumption adopted here, but, because of its uncertainty, in the applications to the solar system, where it turns out fission is impossible, all approximations are made so as to favor fission, and it is assumed that in the actual bodies fission may be immanent long before it is possible in the homogeneous ones. These safeguards and simplifications are possible and easy because it is a negative result which is reached.

The actual problem is not one in which the rate of rotation changes while the density remains constant, though this is the one heretofore treated in the mathematical discussion. In the physical problem the rate of rotation and the density change simultaneously with the shape in such a way that the moment of momentum remains constant. Imposing this condition, we arrive in the case of the spheroids and ellipsoids at relations between the density and respective shapes, the coefficients depending upon the mass

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and the moment of momentum. When the oblateness of the spheroid is given there is but a single density satisfying the conditions, and when the density is given there is but one spheroid satisfying the conditions.

For the applications we assume that an actual celestial body will not be in danger of fission until the corresponding homogeneous incompressible body arrives at the state where the Jacobian ellipsoids branch. The density at this stage is less than one-fourth that at which the pear-shaped figures branch, and actual fission in the homogeneous bodies is certainly beyond this form, if indeed fission into only two bodies is ever possible. With this very conservative assumption we proceed to some calculations.

- (1) We find that the sun can not arrive at this critical stage until its mean density shall have exceeded  $307 \times 10^{11}$  on the water standard. This corresponds to an equatorial diameter of the sun of about 22 miles.
- (2) We find that the sun can not become so oblate as Saturn is now until its mean density shall have exceeded  $148 \times 10^{10}$  on the water standard. This corresponds to an equatorial diameter of the sun of about 75 miles.

Since even the latter density is impossibly great we conclude that the sun will never become so oblate as Saturn is now, and that it will always be more stable than Saturn is now.

- (3) We find that Saturn can not arrive at the critical stage at which the Jacobian ellipsoids branch until its mean density shall have become 21 times that of water. This corresponds to a polar diameter of 16,500 miles and an equatorial diameter of 28,400 miles. We conclude because of the great density demanded that Saturn will never suffer fission.
- (4) We assume that the earth and moon were once one mass and get their original moment of momentum from its present value. In computing it, however, we make certain approximations so as to get it too large and thus favor the conclusion of fission, then we add to it the maximum amount the sun's tides can have taken from the earth, and finally we add 25 per cent for fear there may be some unknown sensible factors omitted. Then we find that this hypothetical earth-moon mass could not get even to the critical point where the Jacobian ellipsoids branch until its mean density became 215 times that of water, or about 40 times the present mean density of the earth and moon. It would not become even so oblate as Saturn is now until its density had become 10.4 times that of water. Therefore we conclude that the hypothetical case was false, and that the moon has not originated by fission from the earth in this way.
- (5) In applications to the binary stars the results are less definite because of the meager data regarding these systems. But assuming that fission in stars will occur when the Jacobian ellipsoids branch in the corresponding homogeneous masses, we find for the density  $\sigma$  in terms of water at the time of fission when the two stars are of equal mass

$$\sigma < \frac{0.016}{P^2}$$

where P must be expressed in mean solar days. Even though fission should not occur until the density is ten times this amount (which, if true, makes the evidence against fission in the solar system much stronger), all visual

binaries of two approximately equal masses must have separated, if they have originated by fission, while they were yet in a nebulous state. The results are of the same order so long as the disparity in the two masses of a binary is not very great, and this probably includes all of the visual binaries.

(6) Certain formulas, not connected with the question of fission, were developed for binary systems. If P represents the period in mean solar days,  $\mu$  the ratio of the mass of the star whose spectrum is measured to the mass of the other one, and  $v_1$  the maximum observed radial velocity expressed in kilometers per second, then the sum of the masses expressed in terms of the sun's mass must satisfy the relation

$$m_1 + m_2 \ge \frac{178}{10^8} P v_1^2 (1 + \mu)^2$$

When the spectra of both stars are measurable, and v represents the maximum relative velocity of the stars, the corresponding formula is

$$m_1 + m_2 \ge \frac{178}{10^8} Pv^3$$

If we let a represent the distance between the centers of a binary pair, and  $\kappa a$  the distance between their surfaces, and suppose they have the same mean density  $\sigma$ , then  $\sigma$  must satisfy the inequalities

$$\frac{8}{100(1-\kappa)^3 P^2} \ge \sigma \ge \frac{2}{100(1-\kappa)^3 P^2}$$

where  $\sigma$  will be expressed in terms of water when P is expressed in mean solar days.

The results obtained by the computations above are quite adverse to the fission theory, in general, except if it is applied to masses in the nebulous state, and seem practically conclusive against it so far as the solar system is concerned, either in the future or past. Perhaps the hypothesis that stars are simply condensed nebulas, which has been stimulated by a century of belief in the Laplacian theory, should now be accepted with much greater reserve than formerly. Up to the present we have made it the basis not only for work in dynamical cosmogony but also in classifying the stars. It may be the time is ripe for a serious attempt to see if the opposite hypothesis of the disintegration of matter—because of enormous subatomic energies, which perhaps are released in the extremes of temperature and pressure existing in the interior of suns, and of its dispersion in space along coronal streamers or otherwise—can not be made to satisfy equally well all known phenomena. The existence of such a definitely formulated hypothesis would have a very salutary effect in the interpretation of the results of astronomical observations. We should then more readily reach what is probably a more nearly correct conclusion, viz., that both aggregation and dispersion of matter under certain conditions are important modes of evolution, and that possibly together they lead in some way to approximate cycles of an extent in time and space so far not contemplated. CONTRIBUTIONS TO COSMOGONY AND THE FUNDAMENTAL PROBLEMS OF GEOLOGY

# THE BEARING OF MOLECULAR ACTIVITY ON SPONTANEOUS FISSION IN GASEOUS SPHEROIDS

BY
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# THE BEARING OF MOLECULAR ACTIVITY ON SPONTANEOUS FISSION IN GASEOUS SPHEROIDS.

It is a familiar view that a rotating spheroid of gas may, by cooling and shrinking, so far accelerate its rate of rotation as to cause its own separation into two or more parts. The resulting parts are assigned various relative values, and the separated masses are given different forms, ranging from fragments and rings to subequal masses. This view of possible self-partition has found expression in various cosmogonic conceptions from the nebular hypothesis to the formation of binary stars.

To consider the bearings of molecular activity in a representative case, let a spheroid of gas be chosen whose mass is comparable with that of the solar system and whose volume is such as may be hypothetically assigned it. Let its rate of rotation at the outset be such that the value of gravitation at the equatorial surface is greater than the centrifugal component of rotation. Let cooling follow, in consequence of which the rate of rotation will be progressively accelerated. Let it be assumed—as has usually been done—that the rate of rotation would at length reach such a velocity that separation in some form would take place regardless of any question as to the manner of its realization. Our question relates to the effect of molecular activity on the transition from an undivided spheroid to a spheroid divided in some way, whether by massive fission, into larger or smaller fractions, or by individual molecules.

In a body whose molecules are bound together into a coherent mass, such parts as may be affected by like general stresses are properly treated as units, within the limits of cohesion, but in a body whose molecules possess all degrees of freedom, and which act with complete individuality, the treatment may with special appropriateness be based on the molecule as the unit. Molecular action in a gaseous spheroid consists of encounters or quasi-encounters, and of rebounds or quasi-rebounds along free paths between the encounters. Within the mass, the excursions and encounters of the molecules give rise to an effect equivalent to viscosity which influences the movement of one part of the gaseous mass upon another part, and may perhaps have given rise to an impression of coherence; but on the outer border of the mass—the critical portion in this case—this effect becomes a vanishing quantity, and individuality of action is dominant.

According to the laws of gaseous distribution, the density of a gaseous spheroid, when controlled solely by its own gravitation, declines from a maximum at the center progressively toward the surface, where the limit of gaseous tenuity is reached and an ultra-gaseous state supervenes. The transition from the gaseous to the ultra-gaseous state is the critical factor in the case, since it is at the extreme surface of the gaseous mass that the

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centrifugal component of rotation first comes into equality with the centripetal force of gravitation and constitutes a condition precedent to the separation of any mass of gas as a body.

In the depths of the gaseous spheroid the paths between encounters may be assumed to be relatively short and hence straight, since gravitation can not sensibly affect paths of brief duration. At higher levels, the free paths grow progressively longer, and at length horizons may be reached at which the attenuation permits free paths of such length and duration that they may be appreciably curved by the gravitation of the spheroid. At still greater heights the attenuation reaches such a degree that curved paths come to dominate and, at a certain stage of rarity, a portion of the molecules rebounding from encounters in outward directions, find no molecules in their paths, and therefore hold on their courses until arrested and turned back by gravitation, if its force be sufficient, or else they pass on beyond the limit of the spheroid's control. Theoretically, under the Boltzman-Maxwell law of molecular distribution, a certain small percentage of molecules should reach the parabolic velocity of the spheroid and escape, but for the purposes of the present discussion this fraction need not be considered independently of a larger class to be described presently, with which it may be merged as having like influence on the moment of momentum of the spheroid.

Such of the outward-bounding molecules as are arrested by the spheroid's gravitation obviously turn back toward the spheroid without a reversing encounter and thus describe elliptical loops. In this they differ markedly from the molecules in the depths of the gaseous spheroid, whose paths are sensibly straight and whose courses are terminated by encounters at either end. In the elliptical courses the outward movement is terminated by a gradual decline in the molecule's speed until its outward progress is reduced to zero, when there follows a new movement inward accelerated by gravitation.

If the to-and-fro, collisional activity of molecules constitutes the essential characteristic of a gas, the outer border of the strictly gaseous part of the spheroid should be placed at the transition zone where the molecules cease to-and-fro passages between encounters and begin to describe elliptical loops limited outward by gravitation, but this demarcation is rather a matter of convenience than an essential in the consideration of the modes of action.

In the course of their outgoing and incoming movements, the molecules pursuing elliptical paths are subject to collision with one another. The phases of such encounters may vary indefinitely and the velocities of the rebounding molecules may represent an indefinite variety of interchanges of kinetic energies. Inspection shows that some of these molecules must rebound toward the gaseous spheroid, that some must take distinctively new elliptical paths, while a certain proportion will inevitably be thrown into courses more or less tangential to the surface of the spheroid, and some of these may have sufficient velocities to assume orbits about the spheroid, and thus form

<sup>&</sup>lt;sup>1</sup> This distinction has been drawn by G. Johnston Stoney, Astrophys. Jour., vol. XI, 1900, pp. 251 and 325, and elsewhere.

a revolutional system of molecules dynamically independent of the spheroid, except that they act as minute satellites.

In a stationary spheroid the rebounds that give rise to revolutional courses are as likely to take one direction as another, and if the mass of the spheroid be great, the number of molecules which will acquire revolution from molecular activity alone may be neglected in this discussion.

But in a spheroid in a state of rapid rotation, especially a spheroid approaching the critical stage of centrifugal separation, the molecules shot outwards in the direction of rotation will start with the sum of the common velocity of rotation and the individual velocities acquired from the last encounter, while the molecules shot in a direction opposite to the rotation will have only the difference between the common velocity of rotation and the velocity acquired from the last encounter, the meridional component in each case being neglected as immaterial here. It follows from this that when the velocity of rotation is high, the molecules starting from encounters in the direction of the spheroid's rotation will much more largely pass into orbital paths than molecules starting in the opposite direction.

In a spheroid having the mass of the solar system and a radius equal to the radius of Neptune's orbit, the equatorial velocity required for separation by mass is above 5 kilometers per second, while the average molecular velocity of all known molecules, at a temperature of 2000° C. and standard terrestrial pressure, falls below this. The average molecular velocity of most known substances falls much below this even at 4000° C. It seems clear therefore that, for most of the known molecules, the effect of molecular velocity directed backward is merely to destroy a part of their rotational speed, and that they still move forward relative to the center of the sphe-With a spheroid having the solar mass and a radius equal to the distance of the earth from the sun, and hence a separation-speed of nearly 30 kilometers per second, only a very small fraction of the molecules could acquire velocities sufficient to neutralize their rotational velocities at the critical stage of separation. The number of molecules that could acquire the 60 kilometers per second required to neutralize their rotational velocities and add sufficient velocity to give them an orbital course in a retrograde direction must obviously be negligibly small in a case of this kind. Practically all molecules must be regarded as having forward courses with velocities which are either enhanced by being shot forward or retarded by being shot backward.

The velocity of centrifugal separation is practically identical with the velocity of circular revolution about the spheroid in a minimum orbit. Larger orbits involve lower velocities but require additional potential energy and moment of momentum. When the rate of rotation of the spheroid is very near, or essentially at, the critical stage of centrifugal separation, a slight addition to the velocity of an outer molecule in a forward direction, arising from molecular interaction, will give to it a velocity greater than that required for the minimum circular revolution; and before the critical state has been actually reached, all molecules on the equatorial periphery which receive forward impulses of any appreciable amount will have more than the requisite velocity for minimum circular revolution. If all mole-

cules whose projections have forward components are regarded as fulfilling these conditions, nearly half the molecules given outward projections will be included.

Encounters and rebounds in gases under familiar terrestrial conditions range into the billions per second, but encounters are much less frequent in rare gases. Excluding outward flights that do not properly belong to the true gaseous state, the maximum period between encounters is less than the rotation-period of the spheroid, and the average period is much less than that. Since interchanges are thus frequent, all molecules are liable to receive a forward impulse within a brief period.

Molecules which simply receive a forward and outward projection greater than that requisite for free circular revolution about the spheroid do not, however, enter upon free orbits, directly, in most cases, because the paths on which they enter, the orbital in type, normally lead back to their starting-points, and in nearly all cases they cut the spheroid before they return to these points and thus complete a free orbit. If this were universally and inevitably true, the way to free orbits along this line of evolution would be effectually barred. There are three lines of escape from this result, the first and second of which are probably unimportant; the third is probably effective.

- 1. The first is the case in which molecules receive impulses from molecular interaction in lines tangent to the points of impact, and hence take elliptical paths about the spheroid which return tangentially to the points of impact as their peri-spheroidal climax. Their liability to encounter the spheroid is thus limited to these tangential touches which, in the rare condition of the gas at these vanishing points of gaseous organization, will not necessarily involve capture. Such molecules will not, however, be free from collision with the molecules pursuing elliptical loops above the gaseous spheroid.
- 2. By hypothesis, the spheroid is shrinking, and if the rate of shrinkage is appreciable during the free flight of molecules whose paths only slightly cut the surface of the spheroid such shrinkage may leave these paths free, so far as the gaseous spheroid is concerned.
- 3. The two cases just named are perhaps more serviceable in defining conditions where gradations rather than sharp limits prevail than as sources of free orbital paths. The most important case is built upon the action of the ultra-gaseous molecules outside the gaseous spheroid, as limited above. These molecules start from the outer part of the spheroid—strictly, from all depths from which there is an open path outward in the line of their projection—and pursue elliptical courses with return to the spheroid, except in the cases just noted. We have seen that, in the representative case of the solar system, the rotational velocity is so great, relative to the average molecular velocity, that most of the molecules will pursue forward courses, even when directed backward, and hence will be moving in harmonious directions. Considered as independent molecules, they constitute a corona of particles rising in curves, predominantly at low angles, and descending at similar angles to the spheroid. They are liable to collide in these courses and a certain percentage of collisions is inevi-

table. Collisions in the rising parts of the curved courses take precedence in time, and hence in probability, over collisions in the declining courses; for if collision is realized in the first part of the course the molecule is likely to lose its chance in the latter part by being either thrown back to the spheroid by the first collision or else thrown outwards where collisions are less imminent. In any case, the collisions probably result either in an earlier return of the molecules to the spheroid, or in throwing them into new paths, of the orbital type, which will bring them back to this point of last collision and not to the spheroid. This point of collision lies above the spheroid. roid, and does not require the orbit to cut any part of the spheroid, though it may do so in a portion of the cases. The predominant effect will apparently be to drive the outer molecules into larger orbits and throw the inner ones back to the spheroid. Apparently this will be a self-adjusting process, so far as frequency and efficiency are concerned, for the number of molecular flights per unit of time will be cumulative as the acceleration of rotation approaches the critical stage when, as we have seen, any molecular increment forward will lead to quasi-orbital flight. This will increase the contingencies of collision, and hence a cumulative number of molecules will be driven into independent orbits.

Now the most significant element in this process is the partition of moment of momentum that is involved. Each molecule that passes into a free orbit necessarily takes with it more than a mean portion of moment of momentum. Those molecules which make elliptical flights and return to the spheroid without collision carry back whatever moment of momentum they took out, but those thrown into permanent orbits retain, as a rule, not only what they took out but also the additional moment of momentum gained from the collisions which gave these free orbits. It follows that every molecule that goes into a free orbit takes a disproportionate amount of the moment of momentum of the spheroid and thus reduces its rotation, or else retards its increase of rotation, to that extent.

If the quantitative value of this loss of moment of momentum by the spheroid could be compared with the increment of rotation assignable to shrinkage, it would be possible to determine whether the spheroid could ever, under these conditions, reach the critical stage requisite for the separation of any portion of its mass bodily. A mode by which a rigorous demonstration can be reached has not yet been found, but, from the nature of the case, I entertain, with others, the view that the separation must take place molecule by molecule, and it seems to me inevitable that these molecules must go into orbits each carrying an excess of moment of momentum at the expense of the spheroid, and hence that the critical stage of exact balance between the centrifugal and centripetal factors of the spheroid is never reached. If so, bodily separation is excluded by the conditions of the case.

The conviction that such rotating gaseous spheroids must shed portions of their matter molecule by molecule, if they do so at all, has long been held by students of the subject, but I am not aware that the loss of moment of momentum from the spheroid has been urged as a reason why the critical state prerequisite to bodily separation may not be attainable.

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# CONTRIBUTIONS TO COSMOGONY AND THE FUNDAMENTAL PROBLEMS OF GEOLOGY

# GEOPHYSICAL THEORY UNDER THE PLANETESIMAL HYPOTHESIS

BY
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# GEOPHYSICAL THEORY UNDER THE PLANETESIMAL HYPOTHESIS.

#### SYNOPSIS.

This paper is devoted mainly to a quantitative study of that portion of the earth's internal energy which is supposed to have been derived from the mechanical energy of a primitive system of planetesimals, of its transformation into thermal form during the epoch of accretion, and its subsequent redistribution by conduction.

In Part I a theory initiated by Fisher is developed on the basis of the Laplacian law of density, together with certain auxiliary assumptions. Formulas and tables are given showing the variation of dimensions and internal densities of the mass during the epoch of accretion, the differential effect of deposit of a stratum on the size and moment of inertia of the mass, and the deformation of mass-elements accompanying the resulting compression. Determination, under alternative secondary postulates, of the original distribution of temperature produced by the compression and its redistribution by conduction shows the existence of a characteristic zone of rising temperatures during the earlier stages.

Part II comprises an inquiry as to what changes in the results of Part I are produced by changes in the secondary hypotheses employed and a critical examination of the latter. The computed masses of the nucleus at various stages of accretion are compared with the observed masses of the smaller planets in the solar system. The previous theory is reviewed, with the substitution of Roche's formula for the density; and to serve as basis of comparison, certain other laws of density are deduced to satisfy special conditions.

Criticism in the light of general thermodynamics leads to a recognition of the theory given as possibly an extreme view, referring to a substance where the work of compression is mainly frictional.

In Part III is outlined a contrasting theory for the case of a substance such that the work of compression is done mainly against volume-elasticity, under the assumption that the successive strata deposited at the surface are reduced to uniform entropy by free radiation while exposed. The thermal phenomena in this case are compared with those under the conditions of Part I.

## INTRODUCTION.

The following studies were undertaken at the suggestion of Prof. T. C. Chamberlin, as auxiliary to the development of the hypothesis put forward by him as to the origin of the earth by planetesimal accretion, a main object being to secure quantitative inferences which might aid in forming a judgment regarding the probable efficiency of thermal energy, whose source is gravitational, as an agent of geological importance under the restrictions imposed by the hypothesis. Experimental evidence regarding the behavior of substances under the enormous temperatures and pressures met with in the interior of cosmic bodies must be considered almost wholly lacking, and derived by highly uncertain extrapolation from determinations made within the limited range accessible to laboratory measurement. Precise conclusions based on accurate observed data could therefore not be looked for, but it was felt that it should be possible to deduce with some confidence at least the order of magnitude and general features of the thermal phenomena of gravitational origin, under the conditions assumed by the hypothesis in question, when supplemented by certain minor hypotheses.

The general hypothesis assumes that the earth, in common with other bodies of the solar system, was formed by the accretion of planetesimal masses, more or less similar in chemical composition, at least when considered on a large scale, so that the more important local differences in the body of the resulting planet are to be ascribed to differences in physical condition, chiefly in pressure and temperature; and that the history of the earth in this aspect comprises two main epochs, the earlier one of growth by accretion, first at a rapid, and later at a declining rate, shading into the subsequent longer period of relative quiescence and constancy of mass, accompanied by a gradual redistribution and partial loss of a store of thermal energy derived from the primitive mechanical energies of the system.

According to the mode of transformation this energy may be treated as mainly of three kinds: (1) that which is stored in the underlying mass, through the progressive static compression which accompanies the deposition of the successive layers at the surface; (2) that derived directly from the kinetic energy of the masses impinging on the surface, through the viscous damping of waves and vibrations due to the impacts; (3) that derived in a similar way from motions which arise from the continual disturbance of equilibrium produced by the surface accretions, independently of the momentum of impact.

To trace out exactly the final distribution of the second and third kinds would be a matter of forbidding difficulty, even if an acceptable assumption could be made regarding the precise law of accretion. No attempt will be made here to account for the third, but from estimates made in the sequel, where attention is confined to the first two, it would appear to be a rather small portion of the whole, being in fact under a certain special set of conditions strictly zero.

As to the second kind, however, the energy of impact, a useful estimate can be made very simply if it be assumed that the single ideal substance contemplated is highly viscous. For in such cases the motions produced by an impact do not travel far from their point of origin before being practically wiped out by friction, thus exhibiting a kind of mechanical radiation of the energy brought in kinetic form by the impinging mass, but in such a way that frictional absorption confines the distribution of that energy to the neighborhood of its source. This sort of process would be closely imitated if the surface structure were that of a loose aggregation of small masses, even if the latter were perfectly solid. It is clear, therefore, that after the transformation the impinging mass retains only a small part of its own original energy, but it secures a certain compensation from the masses whose deposition occurs in time and place near its own. Now, when the average or normal energy of impact per unit-mass does not vary sensibly during the time required for depositing a layer whose thickness is somewhat in excess of the radius of influence implied above, then the compensation may be regarded as practically exact, except as affected by direct radiation into space during the time that the mass remains exposed.

With this interpretation it seems a fair equivalent to assume that each planetesimal mass retains its own primitive kinetic energy after impact in thermal form, but immediately loses a portion by ordinary radiation before it is covered up. This setting of the matter will be accepted hereafter, and it will be further assumed that the process of accretion, though slow enough to permit the loss of a large portion of the heat of impact by immediate radiation, is yet sufficiently rapid so that internal conduction has not time to modify sensibly the distribution of heat arising from compression before the growth is complete.

It may also be supposed that in connection with high viscosity the mass would possess sufficient plasticity to enable its own gravitation to keep it in a condition approaching hydrostatic equilibrium, with an approximately spherical form, aside from the secondary effects of rotation and consequent polar flattening; for it is supposed that in the long run the accretion would be practically equable over the whole surface and that the effects of temporary inequalities of serious magnitude would be quickly obliterated.

It is well understood, by analogy with the behavior of such materials as wax and pitch, that the combination of plasticity and viscosity, such as here contemplated as appearing under slow changes, is in no way inconsistent with the appearance of extreme rigidity under the action of sudden or rapidly varying forces. It should be noted, however, that a satisfactory theory as to the history of the earth's dominant surface features seems to require that to the earth-substance be attributed a rigidity sufficient to allow the alternate accumulation and subsidence of shearing strains, deep in the body of the earth, to such an extent that the periods involved, though short perhaps in comparison with the durations implied in phenomena of thermal conduction in bodies of cosmic size, are nevertheless of higher order than the periods of precession, nutation, and tidal phenomena, which have hitherto furnished the chief data pointing to the practically perfect extreme rigidity of the rotating earth. The hypothesis of practical fluidity under slow deformation must therefore be understood only as a crude first approximation from a geological point of view. But on account of its simplicity, and because of its occurrence in previous theories of the earth's constitution, it is desired to develop first the consequences of this assumption, leaving for later study the question of the modifications needed to allow for rigidity.

The following developments refer entirely to the simple ideal case of a spherical body, radially symmetric in every essential feature, originating by deposition of successive spherical layers, and maintained under its own gravitation in hydrostatic equilibrium which is at least approximate during the period of growth and practically exact thereafter. All variables representing the physical magnitudes concerned are therefore considered as functions of the time and of the distance from the center of the mass. It is desired to study the primitive distribution of thermal energy due to compression and impact, together with the character and rapidity of the modifications brought about by conduction and radiation.

The term "thermal energy" used in the foregoing refers to the entire intrinsic energy of the substance as depending on pressure, density, and temperature; part being the stored or latent energy of the compressional strain, the remainder appearing in a corresponding augmentation of temperature. It is the latter portion only which is subject to direct transfer by pure conduction, though its redistribution in that way, through alteration of the geometric distribution of the mass by thermal expansion and contraction, may lead to the redistribution also of the energy of strain, accompanied in general by further transformation of energy from gravitational to thermal form. The character of the phenomena might easily vary radically with variations in the relative importance of these two portions of the intrinsic

energy, without inconsistency with the general hypothesis.

It is thus essential, for the construction of a definite theory, to include further assumptions as to the thermodynamic properties of the earth-substance, which should cover three main points: (a) the characteristic equation of the substance or relation between the thermodynamic coördinates—pressure, density, temperature; (b) the form of the intrinsic energy as a function of these coördinates; (c) the value of the thermal conductivity in terms of the same variables. Auxiliary coefficients such as specific heats, thermal expansion, and compressibility can then be deduced and the assumptions checked or numerical parameters determined by means of observations or estimates of these physical magnitudes in the case of substances at the earth's surface. It is evident, from the number of these secondary hypotheses needed, that any sharply crucial test of the main hypothesis from the present point of view is out of the question; all that can be done is to form a judgment as to its plausibility in accounting for the play of thermal and gravitational forces in geologic history, by developing several alternative suppositions on these secondary points.

### GENERAL EQUATIONS; NOTATION; NUMERICAL CONSTANTS.

The following notations will be used throughout, and special values of the variable referring to the center and surface of the earth denoted by subscripts 0, 1, respectively:

**d** = loss of potential energy in cont = time.traction from infinity. r =distance from center. E = total energy of compression.x=r/r,.  $\rho = \text{density.}$ e = energy of compression per unitp = pressure.mass. J =mechanical equivalent. m =mass within radius r. k =constant of gravitation. H =modulus of cubic compression. g = acceleration of gravity.  $\sigma$  = specific heat.  $\dot{V}$  = gravitation potential.  $\theta$  = temperature.  $\lambda = conductivity.$ 

Numerical values are given, unless otherwise stated, in terms of the units centimeter, gram, second, and centigrade degree, for convenience in using published data on the absolute values of the physical constants; and are based chiefly on the following assumed constants, unless expressly stated:

Total radius 
$$r_1 = 6.370 \times 10^8$$
 mean density  $\rho_m = 5.516$ 

surface gravity  $g_1 = 981$ 

From these are obtained the following:

volume =  $1.083 \times 10^{27}$  total mass  $m_1 = 5.972 \times 10^{27}$   $k = 6.665 \times 10^{-8}$ 

Further are assumed:

$$\rho_1 = 2.70 \text{ to } 2.75 \text{ (estimated average for surface-rock)}$$
 
$$J = 4.2 \times 10^7 \qquad H_1 = \text{about } 4 \times 10^{11} \qquad \sigma_1 = \text{about } 0.2 \qquad \lambda_1 = \text{about } 0.005$$

As stated above, it is necessary to supplement the general hypothesis by certain assumptions as to the physical properties of the earth-substance, in particular the form of the characteristic thermodynamic surface:

$$F(p,\rho,\theta)=0 \tag{1}$$

and the form of the intrinsic energy, conveniently an expression of the type:

$$e = f(\rho, \theta) \tag{2}$$

The fundamental equations forming the basis of the theory may then be grouped in two classes, related to two curves, not necessarily identical, on the surface (1). The first curve belongs to the actual distribution of the physical magnitudes within the earth at a given time, its projection in the p- $\rho$  plane being determined in parameter form by the values of p and  $\rho$  as functions of r. The second curve corresponds to the path of compression traversed by a particular mass of the substance from the time of its deposition to the time when the growth of the planet is complete, and is practically an adiabatic curve if the accretion and consequent compression are relatively rapid, as is here supposed.

In the first class come the equations:

$$\frac{dp}{dr} = -g\rho \qquad \text{with } p_1 = 0 \tag{3}$$

where

$$g = \frac{km}{r^2} \tag{4}$$

and

$$m = 4\pi \int_{0}^{T} \rho r^2 dr \tag{5}$$

which express the condition of hydrostatic equilibrium and yield the important relation:

$$\frac{d}{dr}\left(\frac{r^2}{\rho}\frac{dp}{dr}\right) + 4\pi k\rho r^2 = 0 \tag{6}$$

subject to the conditions

$$p_1=0$$
 ,  $\frac{dp}{dr}\Big)_0=0$ 

To these must be added the expression for the potential energy exhausted during contraction from infinity:

$$\Phi = \frac{1}{2}k \int V dm = 2\pi k \int_{0}^{r_1} \rho V r^2 dr \tag{7}$$

where

$$V = \frac{4\pi}{r} \int_0^r \rho r^2 dr + 4\pi \int_r^{r_1} \rho r dr$$
 (8)

the latter being equivalent to

$$k\frac{dV}{dr} = -g \tag{9}$$

with

$$V_0 = 4\pi \int_0^{r_1} \rho r dr$$
 or  $V_1 = \frac{m_1}{r_1}$ 

Let

$$u = V - V_1 \tag{10}$$

then equations (9), (3) give

$$\frac{d}{dr}\left(r^2\frac{du}{dr}\right) + 4\pi\rho r^2 = 0\tag{11}$$

where  $\rho$  may be considered expressed in terms of u or r, since u is necessarily and  $\rho$  most probably a monotonic function of r in the concrete case.

The preceding equations then suffice to determine in terms of r all variables involved, if supplemented by a single hypothetical equation, such as an expression for  $\rho$  in terms of r or a relation between p and  $\rho$ .

The second class of equations, in addition to (1), (2), includes the equations of the particular path of compression in question, together with the expression for the work done in compressing unit-mass:

$$e = \int_{\rho_1}^{\rho} \frac{p}{\rho^2} \, d\rho \tag{12}$$

which gives through integration by parts the relations

$$e\rho + p = \rho s$$
  $d(e\rho) = sd\rho$  (13)

the useful auxiliary variable s being defined by

$$s = \int_{\rho_1}^{\rho} \frac{H}{\rho^2} d\rho \tag{14}$$

where the elastic bulk-modulus H is

$$H = \rho \, \frac{dp}{d\rho} \tag{15}$$

The limits of the integrals correspond to the supposition that the matter is compressed from surface density and zero pressure. With  $\epsilon$  so determined, and expressed in terms of r by means of equations of the first class, the total energy of compression is

$$E = \int e dm = 4\pi \int_{0}^{r_{1}} e \rho r^{2} dr = -\frac{4\pi}{3} \int_{0}^{r_{1}} s \rho^{2} \frac{d\rho}{dr} dr$$
 (16)

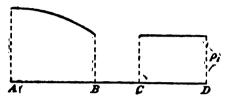
the last form being obtained by integration by parts and equation (13). It may be noticed that the quantities ku and s are of the same physical dimensions, but with distinct theoretical setting; in case, however, the two paths on the thermodynamic surface are identical, they are equal at every point in the body. In this special case the value of E may be given as

$$E = \frac{4\pi k}{3} \int_{0}^{r_1} r^2 (V_1 - V) \frac{d\rho}{dr} dr$$

An essential feature of the present hypothesis is the necessity of supposing that most of the energy of impact is wasted by immediate radiation, so that the compressional energy whose total is E plays the main part in the succeeding phenomena. It is therefore important for purposes of comparison to determine what ratio the quantity E bears to the total energy transformed.

An idea on this point may be obtained by considering the case of a planet formed by condensation of a primitive homogeneous sphere of density  $\rho_1$ . Suppose that a particle at distance r from the center in the completed planet lay momentarily at distance r' when deposited at the temporary surface, and in the homogeneous sphere would lie at distance  $r_h$ , these being subject to the inequalities  $r_h > r' > r$ . It may be considered that the particle fell

from distance  $r_{\lambda}$  to distance r', striking the surface, and then being covered up more and more deeply, settled finally to distance r. The diagram gives an idea of the distribution of density at the instant of deposition of that particle, A being the center, the part CD along the radius referring to the



homogeneous spherical shell which is being drawn up to supply surface deposits at B, BC the empty region through which the particles are falling, and AB the radius of the partially formed planet, the variation of density within which is determined by the condition of equilibrium under a definite law of compressibility.

Since the mass already deposited is m, the energy of impact per unitmass is under these special conditions:

$$e_i = km \left( \frac{1}{r'} - \frac{1}{r_k} \right) \tag{17}$$

where  $m, r', r_h$  are to be thought of as functions of r; then the total energy of impact is

$$E_{i} = 4\pi k \int_{0}^{r_{1}} \rho m \left(\frac{1}{r'} - \frac{1}{r_{h}}\right) r^{2} dr$$
 (18)

The quantities E and  $E_i$  are portions of the potential energy  $\bullet - \bullet_h$  exhausted during condensation of the homogeneous sphere to a condition of density matching that of the completed planet,  $\bullet_h$  being the value of  $\bullet$  for a sphere of assigned mass  $m_i$ , and uniform density  $\rho_i$ , and determined by

$$\Phi_{h} = \frac{3}{5} k \frac{m_{1}^{2}}{r_{1,h}} \qquad r_{1,h}^{3} = \frac{3m_{1}}{4\pi\rho_{1}}$$
 (19)

The remainder of the energy  $\Phi - \Phi_h$ , if any, is to be treated as of the third kind named above; but in case the equilibrium in the mass already deposited at each moment of the process is adiabatic, so that the two thermodynamic curves mentioned are identical, it seems probable that this third kind does not exist, and the total amount  $\Phi - \Phi_h$  transformed is completely accounted for as  $E + E_t$ . This is later proved to be the case for one particular pressure-density law. In any case it is of course not meant that the primitive distribution need be at all like that in the homogeneous sphere mentioned, but any other supposition would modify only the energy of impact, leaving the above point of view still useful as a check on the computation of the compressional portion  $E_t$  this is verified by the expression of  $E_t$  as the difference

$$4\pi k \int_{0}^{r_1} \frac{\rho m}{r'} r^2 dr - 4\pi k \int_{0}^{r_1} \frac{\rho m}{r_h} r^2 dr$$

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the first member being the energy of impact corresponding to parabolic velocities, the second being identical with  $\boldsymbol{\theta}_k$ . The former would correspond to formation from a system of small particles each of density  $\rho_l$ , but infinitely dispersed, so that the potential energy available is  $\boldsymbol{\theta}$ . It should be noted also that the part E is not affected by the existence of velocities in the primitive planetesimals due to attractions other than that of the nucleus on which they fall, and can therefore be treated independently of any supposition as to their distribution and motions previous to the aggregation.

## PART I.—THE THEORY OF FISHER.

#### GENERAL EQUATIONS.

A definite form for the development of the theory has been initiated by Fisher,1 on the basis essentially of three main suppositions as to the properties of the ideal earth-substance. These are: (1) that the path of compression traversed by any particular element of the mass is identical as far as it goes with that defined by the relation between density and pressure within the earth in its final state; (2) that pressure and density are related as specified by the classic law of Laplace; (3) that rise of temperature during compression is proportional to increase of compressional energy, or of work done to produce compression.

For critical purposes it will be necessary to undertake a close scrutiny of these assumptions, as to their agreement with pertinent observed data, and also, in the light of general thermodynamic laws, of their consistency with each other, or at least of the exact interpretation to be accorded them in order to assure consistency. But in view of their close affiliation with the standpoints adopted in many previous studies of the constitution of the earth's interior, it will be worth while to develop their consequences in some detail.

The pressure density law, proposed by Laplace, has been used by many writers on geophysics, partly it would seem on account of its mathematical convenience, being the only one which reduces equation (6) to linear form. It is based on the condition

$$\frac{dp}{d\rho} = h\rho \qquad h = \text{const.} \tag{20}$$

which, when applied to the compression of an individual portion of the mass, gives

$$p = \frac{h}{2} (\rho^2 - \rho_1^2)$$
 (21)

and for equations (12) and (14) the particular forms

$$e = \frac{h}{2} \frac{(\rho - \rho_1)^2}{\rho} \tag{22}$$

$$s = h \left( \rho - \rho_1 \right) \tag{23}$$

Assumption (1), however, which gives s = ku, allows the use of the relation (20) in the differential equation (6) or (11), which reduces to

$$\frac{d}{dr}\left(r^2\frac{d\rho}{dr}\right) + q^2\rho r^2 = 0 \qquad q = \sqrt{\frac{4\pi k}{h}}$$
 (24)

the appropriate solution being

$$\rho = \rho_0 \frac{\sin \beta}{\beta} \qquad \beta = qr \qquad (25)$$

<sup>&</sup>lt;sup>1</sup> Rev. O. Fisher. On Rival Theories of Cosmogony. Am. J. of Sc., x1, 1901, p. 414. <sup>2</sup> Laplace, Mécanique Céleste, book x1, chap. Iv.

leaving the constants  $\rho_0$ , q to be adjusted according to observation and thus determine h indirectly.

Formulas for the principal variables are, then,1

$$m = \frac{4\pi\rho_0}{q^3} \left(\sin\beta - \beta\cos\beta\right) \tag{26}$$

$$g = \frac{4\pi k \,\rho_0}{q} \cdot \frac{\sin \beta - \beta \cos \beta}{\beta^2} \tag{27}$$

$$p = \frac{2\pi k \,\rho_0^2}{q^2} \left\{ \left( \frac{\sin \beta}{\beta} \right)^2 - \left( \frac{\sin \beta_1}{\beta_1} \right)^2 \right\} \tag{28}$$

also

$$V - V_1 = u = \frac{8}{k} = \frac{h(\rho - \rho_1)}{k}$$

whence

$$V = \frac{m_1}{r_1} + \frac{4\pi}{q^2} \left(\rho - \rho_1\right) \qquad \text{or} \qquad V = \frac{4\pi \rho_0}{q^3} \left(\frac{\sin \beta}{\beta} - \cos \beta_1\right) \tag{29}$$

For comparison of the variables p,  $\rho$ , e, with their values at the center, there are the ratios

$$\frac{\rho}{\rho_0} = \frac{\sin \beta}{\beta} \tag{30}$$

$$\frac{p}{p_0} = \frac{\rho^2 - \rho_1^2}{\rho_0^2 - \rho_1^2} \tag{31}$$

$$\frac{e\rho}{e_0\rho_0} = \left(\frac{\rho - \rho_1}{\rho_0 - \rho_1}\right)^2 \tag{32}$$

while the mean density is

$$\rho_{m} = 3\rho_{0} \frac{\sin \beta_{1} - \beta_{1} \cos \beta_{1}}{\beta_{s}^{2}} \tag{33}$$

or in form of power series:

$$\frac{\rho_{m}}{\rho_{0}} = \frac{3}{\beta_{1}^{2}} \left( \frac{2\beta_{1}^{2}}{3!} - \frac{4\beta_{1}^{4}}{5!} + \frac{6\beta_{1}^{6}}{7!} - \cdots \right)$$

The expressions for E and  $\Phi$  take particular forms readily reduced to

$$E = \frac{8\pi^2 k \, \rho_0^2}{q^3} \int_0^{\beta_1} \frac{d}{d\beta} \left\{ \frac{\beta}{2} - \frac{\sin 2\beta}{4} - \frac{2\sin \beta_1}{\beta_1} \left( \sin \beta - \beta \cos \beta \right) + \left( \frac{\sin \beta_1}{\beta_1} \right)^2 \frac{\beta^2}{3} \right\} d\beta$$

$$\Phi = \frac{8\pi^2 k \, \rho_0^2}{q^3} \int_0^{\beta_1} \frac{d}{d\beta} \left\{ \frac{\beta}{2} - \frac{\sin 2\beta}{4} - \cos \beta_1 \left( \sin \beta - \beta \cos \beta \right) \right\} d\beta$$

giving for these total energy values:

$$E = \frac{4\pi^2 k \,\rho_0^2}{q^5} \beta_1 \left\{ 1 + \frac{2\sin^2\beta_1}{3} - 4\left(\frac{\sin\beta_1}{\beta_1}\right)^2 + 3\frac{\sin\beta_1}{\beta_1}\cos\beta_1 \right\}$$
(34)

<sup>&</sup>lt;sup>1</sup> Most of these formulas occur in Fisher's paper, or in antecedent writings where the Laplacian law is used.

$$\mathbf{\Phi} = \frac{4\pi^2 k \; \rho_0^2}{q^4} \; \beta_1 \left\{ 1 + 2 \cos^2 \beta_1 - 3 \frac{\sin \beta_1}{\beta_1} \cos \beta_1 \right\}$$
 (35)

The constants  $\rho_0$ , q, may be determined, for example, so as to give accordance with any assumed values for mean density  $\rho_m$  and surface density  $\rho_{i}$ , or the latter may give place to the condition resulting from observations of precession and polar flattening, which, according to somewhat uncertain theory, indicate for the angle  $\beta_1$  a value in the neighborhood of 140°. The following computations are based on the assumed value 141.8°, together with the numerical constants as listed in the introduction, giving the following table under the assumed law:

$$\begin{array}{lll} \beta_1 = 2.475 = 141.8^{\circ} & q = 3.885 \times 10^{-6} \\ \rho_1/\rho_0 = 0.25 & H_1 = 4.096 \times 10^{11} \\ \rho_1 = 2.717 & E = 3.620 \times 10^{26} \\ \rho_0 = 10.87 & \theta = 2.456 \times 10^{26} \\ h = 5.549 \times 10^{10} & \theta_h = 1.768 \times 10^{26} \end{array}$$

The resulting value of the surface density  $\rho_i$ , though perhaps rather small, accords fairly well with estimates of the mean density of superficial strata, and an additional check on the applicability of the density-law in question is found, as pointed out by Fisher, in the fact that the surface value H<sub>1</sub> of the elastic bulk-modulus ranges close to values found by direct measurement.2

The accompanying tables, then, show the distribution of the principal magnitudes at the close of the epoch of aggregation. The columns referring to  $\rho$ , p, g are of course not novel, but are inserted for the sake of having all computations based on an uniform set of numerical constants.

TABLE 1.

$r/r_1$	ρ	P/P1	P/Po	f(x)	g	9/91
0.00	10.874	4.002	1.0000	1.0000	0.0	0.000
.05	10.846	3.992	.9974	.9975	96.3	.098
.10	10.763	3.961	.9898	.9900	191.8	.196
.15	10.625	3.911	.9772	.9776	286.0	.292
.20	10.435	3.841	.9596	.9604	377.3	.385
.25	10.193	3.751	.9374	.9385	465.1	.474
.30	9.902	3.644	.9106	.9120	548.8	.559
.35	9.564	3.520	.8796	.8813	627.4	.640
.40	9.183	3.380	.8445	.8464	700.3	.714
.45	8.761	3.225	.8057	.8077	767.0	.782
.50	8.303	3.056	.7636	.7656	826.7	.843
.55	7.814	2.876	.7186	.7204	879.1	.896
.60	7.296	2.685	.6710	.6724	923.8	.942
.65	6.755	2.486	.6212	.6221	960.4	.979
.70	6.195	2.280	.5697	.5700	988.6	1.008
.75	5.621	2.069	.5170	.5166	1008.3	1.028
.80	5.039	1.855	.4634	.4624	1019.6	1.039
.85	4.452	1.639	.4095	.4080	1022.3	1.042
.90	3.867	1.423	.3556	.3540	1016.7	1.036
.95	3.287	1.210	.3023	.3011	1002.8	1.022
1.00	2.717	1.000	.2499	.2500	981.0	1.000

<sup>&</sup>lt;sup>1</sup> Tisserand, Méc. Cél., п, р. 235. <sup>2</sup> Fisher, *loc. cit.*, р. 417; also Kelvin and Tait, Natural Philosophy, п, р. 415.

In table 1, fifth column, f(x) stands for  $(1-\frac{1}{2}x^2)^2$ , tabulated for comparison because of its occurrence in an approximate formula for the density used later. The maximum value of g occurs at x=0.8411, or about 630 miles below the surface.

TABLE 2.

<i>r/r</i> <sub>1</sub>	10—13 p	<b>P/P</b> 0	10 <sup>-19</sup> H	$H/H_1$	10-0€	e/e0	5e/J
.00	3.076	1.000	6.561	16.02	169.8	1.0000	20,210
.05	3.059	.995	6.527	15.93	169.0	.9957	20,120
.10	3.009	.978	6.428	15.69	166.9	.9830	19,870
.15	2.927	.952	6.265	15.29	163.3	.9619	19,440
.20	2.816	.916	6.042	14.75	158.4	.9329	18,850
.25	2.677	.870	5.765	14.07	152.1	.8961	18,110
.30	2.515	.818	5.440	13.28	144.6	.8520	17,220
.35	2.333	.759	5.076	12.39	136.0	.8011	16,190
.40	2.135	.694	4.679	11.42	126.3	.7441	15,040
.45	1.925	.626	4.259	10.40	115.7	.6814	13,770
.50	1.708	.555	3.826	9.34	104.3	.6141	12,410
.55	1.489	.484	3.388	8.27	92.2	.5434	10,980
.60	1.272	.414	2.953	7.21	79.7	.4697	9,490
.65	1.061	.345	2.532	6.18	67.0	.3945	7,970
.70	.860	.280	2.129	5.20	54.2	.3191	6,450
.75	.672	.218	1.753	4.28	41.6	.2452	4,960
.80	.500	.162	1.409	3.44	29.7	.1749	3,530
.85	.345	.112	1.100	2.69	18.7	.1105	2,230
.90	.210	.068	.830	2.03	9.5	.0559	1,130
.95	.095	.031	.599	1.46	2.7	.0162	330
1.00	.000	.000	.410	1.00	0.0	.0000	0

The second and fourth columns give the values of the pressure and bulk-modulus in millions of atmospheres, an atmosphere being taken as one megadyne per sq. cm., while the seventh column gives the specific compressional energy in billions of ergs per gram. The last column is added for the sake of vividness of interpretation in terms of temperature, being the measure of the thermal equivalent of e in centigrade degrees, under specific heat one-fifth that of water.

Of the total store of potential energy  $\Phi$ , it appears that 72 per cent is accounted for by  $\Phi_{h}$ , which would be the energy exhausted if a system of planetesimals, originally infinitely dispersed, united to form a homogeneous sphere of density  $\rho_{1}$ ; this portion is to be thought of as energy of impact. Of the remaining portion  $\Phi - \Phi_{h}$ , the compressional energy E accounts for 53 per cent.

It remains to be determined whether the excess of  $\Phi - \Phi_h$  over E is also to be ascribed to energy of impact. That a part at least must be so considered follows from the assumed character of the actual aggregation. For when a given particle impinges on the momentary surface, the mass already gathered has condensed, under its own gravity, to smaller dimensions than it would occupy in the homogeneous sphere; the radius being smaller, the velocity of impact is greater than would be the case under the attraction of the same mass in homogeneous form with the minimum density  $\rho_i$ . For a particle having any assigned position in the completed planet the attracting mass within can be computed by (26). But the velocity of impact depends also on the momentary radius of that mass, before it has been further con-

densed by deposition of the remaining layers, so that in order to determine the total amount and distribution of the energy of impact it is necessary to know how the compression advances in the existing nucleus as material is deposited at its surface.

### HISTORY OF THE COMPRESSION.

It is possible, under the foregoing assumptions, to trace such a history of the accretion, if it be supposed that the equilibrium of the mass is maintained at each stage of the process. For if the preceding equations can be accepted as approximate representation of the action of the earth-substance under compression, to a similar approximation equation (20) must be viewed as representing a physical property of that substance, independent of the dimensions of the mass into which it is aggregated, the constants h, q being physical constants of the material. The distribution of density in a body of any size is then represented by equation (25), without change in the value of q, but with the maximum value of  $\beta$  chosen to agree with the total radius, and with central density such as to give the surface density the fixed value  $\rho_1$ . The distance of any particle from the center is then fixed by the angle  $\beta$ , which is the measure of that distance in terms of a unit of 1/q centimeters, or about 1,600 miles.

Let  $r_s'$  be the radius of the nucleus already formed at a certain epoch, and  $r_s$  its radius when compressed under the total load afterwards deposited; let r', r be the central distances of any interior particle at the same epochs; then  $r_s'$  is to be determined as a function of  $r_s$ , and r' as a function of r and  $r_s$ ; the latter function describing the history of the condensation in the sense that it fixes the position of any assigned particle at any epoch, if the epoch is specified by the final location of the particles which then lay at the surface. A translation into time-relations could then be made for any postulated law of variation in the rate of accretion. Let  $\rho_0'$  be the central density at the earlier epoch. For brevity put

$$B = \frac{\sin \beta}{\beta} \qquad C = \sin \beta - \beta \cos \beta \qquad (36)$$

to be indexed, like the various values of  $\beta$ , by analogy with the values of r to which they refer, as in equation (25).

By equation (26) the identity of the masses within the radii  $r_*$ ,  $r_*$  at the respective epochs gives the condition

$$\rho_{\mathbf{o}}' C_{\mathbf{s}}' = \rho_{\mathbf{o}} C_{\mathbf{s}} \tag{37}$$

similarly for the corresponding radii r', r:

$$\rho_0' C' = \rho_0 C \tag{38}$$

and from the constancy of density at the momentary surface

$$\rho_0' B_{\bullet}' = \rho_0 B_1 \tag{39}$$

These equations are to determine the values of  $\rho_{\bullet}'$ ,  $\beta_{\bullet}'$ ,  $\beta'$ , for any assigned values of  $\beta_{\bullet}$  and  $\beta$ , for instance first  $\beta_{\bullet}'$  from (37) and (39) which give

$$\frac{C_{\bullet'}}{B_{\bullet'}} = \frac{C_{\bullet}}{B_1} \tag{40}$$

then  $\rho_{\bullet}'$  from (37) and finally  $\beta'$  from (38). The values of  $\beta_{\bullet}'$  and  $\rho_{\bullet}'$  as functions of  $\beta_{\bullet}$  are given in table 3 below. The former were obtained by interpolation from an extended table giving C/B and  $C/B_1$  as functions of  $\beta$ . To trace the positions of interior particles at different distances and different epochs would require a double-entry table, which could be supplied by equation (38) after  $\rho_{\bullet}'$  has been computed.

by equation (38) after  $\rho_0$  has been computed.

The specific energy of impact, or kinetic energy of a unit-mass falling from infinity to the surface of a nucleus of mass  $m_a$  and radius  $r_a$  is, then,

$$e_i = \frac{km_a}{r'} \tag{41}$$

where by (26) the attracting mass is

$$m_s = \frac{4\pi \, \rho_0}{q^3} \, C_s$$

The values of  $e_i$  are given in table 4, in terms of  $\beta_s$ , which determines the ultimate position of the particle.

The total energy transformed by impact is, then,

$$E_{\epsilon} = 4\pi \int_{0}^{r_{1}} \rho_{\epsilon} \cdot \frac{k m_{\epsilon}}{r_{\epsilon}'} \cdot r_{\epsilon}^{2} dr_{\epsilon}$$

which, since  $\rho_s = \rho_0 B_s$ , is equivalent to

$$E_{\epsilon} = \frac{16\pi^{2}k \, \rho_{0}^{2}}{q^{3}} \int_{0}^{\beta_{1}} \frac{C_{s}B_{s}\beta_{s}^{2}}{\beta_{s}'} d\beta_{s}$$

But by equation (40)

$$\beta_{s'} - \beta_{s'^2} \cot \beta_{s'} = \frac{\sin \beta_{s} - \beta_{s} \cos \beta_{s}}{B_1}$$

whence

$$\frac{C_{\mathfrak{s}'^2}}{\beta_{\mathfrak{s}'^2}B_{\mathfrak{s}'^2}} + \beta_{\mathfrak{s}'^2} = \frac{\beta_{\mathfrak{s}}\sin\beta_{\mathfrak{s}}}{B_1} \frac{d\beta_{\mathfrak{s}}}{d\beta_{\mathfrak{s}'}} \tag{42}$$

Use of this relation to transform the variable of integration from  $\beta_s$  to  $\beta_s'$  gives

$$E_{\epsilon} = \frac{16\pi^{2}k \; \rho_{0}^{\; 2} \; B_{1}^{\; 2}}{q^{5}} \int_{0}^{\beta_{1}} \frac{C_{s'}}{\beta_{s'} B_{s'}} \left\{ \frac{C_{s''}^{\; 2}}{\beta_{s''}^{\; 2} B_{s''}^{\; 2}} + \beta_{s''}^{\; 2} \right\} d\beta_{s'}^{\; 2}$$

where the integrand is expressed entirely in terms of  $\beta_s$ , the upper limit of the integral being unchanged according to (40). The result of the integration is

$$E_{i} = \frac{16\pi^{2}k \; \rho_{0}^{\; 2} \; B_{1}^{\; 2}}{q^{4}} \; \beta_{1} \left[ \frac{(1-\beta_{1} \cot \beta_{1})^{2}}{2} + \frac{1-\beta_{1} \cot \beta_{1}}{2} - \frac{\beta_{1}^{\; 2}}{6} \right]$$

which may be written:

$$E_{i} = \frac{4\pi^{2}k \,\rho_{0}^{2}}{q^{6}} \beta_{1} \left\{ \frac{4\sin^{2}\beta_{1}}{\beta_{1}^{2}} - \frac{6\sin\beta_{1}\cos\beta_{1}}{\beta_{1}} + \frac{8}{3}\cos^{2}\beta_{1} - \frac{2}{3} \right\}$$
(43)

Comparison with (34) and (35) gives the fundamental relation

$$E + E_{\epsilon} = \emptyset \tag{44}$$

showing that under the conditions here assumed the original store of potential energy is entirely accounted for as transformed by impact and static compression. The proof refers to a primitive condition of infinite dispersion, but a similar conclusion would hold for any initial configuration and distribution of velocities provided  $\Phi$  stands for the entire primitive store of energy, potential and kinetic, a variation in which would make an equal change in  $E_{\nu}$  but leave E unaltered.

As represented by the preceding equations the character of the process of accretion, upon a nucleus composed of material of definite compressibility, implies that the deposition of a new layer of given thickness brings about a certain increase of compression of the nucleus and a corresponding sinking of the former surface toward the center; only part of the thickness of the new stratum is thus effective in producing actual increase of geometric dimensions. In order to specify this differential depression numerically, let a factor of depression D be defined as the ratio, to the total thickness of stratum, of the part which sinks below the level of the former surface; then 1-D is the ratio of geometric increment of radius to total thickness of stratum.

For simplicity of notation let  $\beta$  now stand for the angle equivalent of the radius of the nucleus at a given epoch, the mass being by (25) and (26):

$$m = \frac{4\pi \, \rho_1}{q^3} \left\{ \beta - \beta^2 \cot \beta \right\}$$

where  $\rho_1$  is the fixed density of surface rock, so that

$$dm = \frac{4\pi \rho_1}{q^3} \left\{ (1 - \beta \cot \beta)^2 + \beta^2 \right\} d\beta$$

dm being the increment of mass and  $d\beta$  the increment of radius in the angular units defined. If, however, a stratum of the same mass dm were laid down without producing compression of the nucleus beneath, the relation to the total thickness  $\partial\beta$  of the stratum would be given by

$$dm = \frac{4\pi\rho_1}{a^3} \beta^2 \delta \beta$$

From these follows for the depression factor

$$D = 1 - \frac{d\beta}{\partial \beta} = \frac{1}{1 + \left(\frac{\beta \sin \beta}{C}\right)^2}$$
 (45)

where C is defined as in (36). The factor D is tabulated in column 6 of table 3, in terms of  $\beta_{\bullet}$ , which there represents the momentary radius of the free surface.

A similar situation occurs with respect to the effect of accretion on the moment of inertia and period of rotation of the planet. The moment of inertia is

$$I = \frac{8}{3} \pi \int_{a}^{r} \rho r^4 dr$$

or, measured for convenience in terms of a unit equal to  $\frac{8\pi \rho_1}{3q^5}$  C. G. S. units.

 $I = \frac{\beta}{\sin \beta} \int_{0}^{\beta} \beta^{\alpha} \sin \beta \, d\beta$ 

which reduces to

$$I = 2\beta^{0} - \frac{C}{R} (6 - \beta^{2})$$
 (46)

Now, in the same units the stratum itself adds to the moment of inertia the quantity

$$\delta I = \beta^4 \, \delta \beta = \beta^4 \left\{ 1 + \left( \frac{C}{\beta^2 B} \right)^2 \right\} d\beta \tag{47}$$

But this is in excess of the true increment, because the differential condensation diminishes the moment of inertia of the underlying mass. The true increment by (46) is

$$dI = \left\{\beta^4 + \frac{2\beta C}{B} + (\beta^2 - 6) \left(\frac{C}{\beta B}\right)^2\right\} d\beta$$

which may be written:

$$dI = \delta I - 2\beta^{\alpha} K \left( \frac{3K}{\beta} - 1 \right) d\beta \tag{48}$$

where

$$K = \frac{C}{\beta^2 B}$$

giving for comparison:

$$\frac{dI}{\partial I} = 1 - \frac{2K}{\beta} \left( \frac{3K}{\beta} - 1 \right) (1 - D) \tag{49}$$

which is tabulated in column 7 of table 3. Then by combination of equations (45) to (49) may be computed

$$\frac{d \log l}{d \log \beta} = \frac{\beta^6}{l} \cdot \frac{1}{1 - D} \cdot \frac{dl}{\delta l} \tag{50}$$

which gives the ratio of the percentage increase of the moment of inertia to the percentage increase of the radius. This would indicate also the percentage change in the length of the day if the stratum were deposited entirely under normal incidence, or if the moments of momentum of the planetesimals with respect to the existing axis of rotation exactly compensated each other. If, however, it be supposed that variations in the rotation, or even the existence of the rotation, were brought about by lack of such compensation, then the equations allow this effect to be distinguished from that due merely to changes in the moment of inertia.

As illustration may be considered the case of superficial strata deposited when the earth had attained practically its final dimensions, and corresponding therefore to the last entry in the tables. A stratum, for instance, exerting the same pressure as a mercury column of 760 mm. would have a thickness of 3.8 meters; the depression factor D is 0.737; hence that stratum would depress the former surface 2.8 meters, giving actual increase to the radius of only 1 meter. This increase bears to the total radius a ratio  $\frac{1}{6.37} \times 10^{-6}$ , while the value of  $\frac{d \log I}{d \log \beta}$  is 7.08; hence, for the case of normal impact, the corresponding increase of the period of rotation is about  $\frac{1}{9} \times 10^{-6}$  of the whole, or 0.096 of a second for a day of the present length. To increase the period just one second out of 86,164 would require a stratum 39.7 meters thick. The illustration also indicates that under the assumed law of compressibility the mean pressure of the atmosphere is responsible for a diminution of the earth's radius amounting to 2.8 meters.

The preceding computation of pressures and densities has been based on the condition of hydrostatic equilibrium, which for any substance not completely fluid can be considered strictly applicable only in case each portion of the mass is subjected to compression in such a way as to avoid any distortion of shape, which would call into play reactions against shearing stresses. It will therefore be instructive to determine what kind of deformation in the elementary portions of the mass is implied in the foregoing account. In view of the radial symmetry assumed, the distortion at any point in the completed planet may be expressed in terms of a distortion-factor S, defined as the ultimate ratio of vertical to horizontal dimensions of a mass which when first deposited at the surface was cubical.

The ratio of final to initial horizontal dimensions is  $\beta_s/\beta_s'$ , being the same as the ratio of radii of two spheres passing through the same particles at the respective epochs. The vertical or radial ratio in the same sense is  $\frac{\rho_1\beta_s'^2}{\rho_s\beta_s^2}$ , since conservation of the mass of a stratum implies

$$\rho_1\beta_*'^2\delta\beta' = \rho_*\beta_*^2\delta\beta$$

if  $\delta \beta'$ ,  $\delta \beta$  represent the respective thicknesses. These give for the distortion-factor

$$S = \frac{\rho_1}{\rho_s} \left( \frac{\beta_s'}{\beta_s} \right)^2 \tag{51}$$

whose value at various depths is given in column 5 of table 4, which shows that the vertical compression throughout exceeds the horizontal, the difference being most marked about one-fourth of the way to the center, where the ratio is 0.824. This would be a violent deformation for a body with perceptible rigidity, but may be admitted in the present theory if it be supposed that under extremely slow changes the substance is practically plastic, even if highly viscous. The chief uncertainty would then relate to the energy of compression, which should take account of the work done against viscosity under shear. Further comment on this matter will be reserved for another place.

TABLE 3.

<u>β</u> <sub>θ</sub>	$\frac{\beta_{\delta'}}{\beta_1}$	Po'	m <sub>e</sub>	ge' g <sub>1</sub>	D <sub>6</sub> '	<u>dI</u>	d log I d log β
0.00	0.000	2.72	0.00	0.000	.000	1.000	5.00
.05	.079	2.73	.000245	.003	.004	.999	5.00
.10	.158	2.79	.00195	.012	.017	.993	5.01
.15	.235	2.89	.00656	.027	.038	.985	5.02
.20	.311	3.00	.01538	.050	.067	.973	5.06
.25	.384	3.17	.02963	.077	.102	.958	5.10
.30	.454	3.38	.05035	.111	.144	.940	5.14
.35	.520	3.64	.07834	.151	.191	.920	5.20
.40	.582	3.95	.1142	.196	.241	.897	5.27
.45	.641	4.31	.1583	.247	.294	.873	5.35
.50	.695	4.72	.2107	.303	.348	.847	5.45
.55	.744	5.19	.2711	.364	.402	.821	5.56
.60	.789	5.71	.3390	.430	.455	.794	5.69
.65	.829	6.28	.4136	.499	.504	.768	5.83
.70	.865	6.90	.4938	.571	.550	.744	5.99
.75	.896	7.55	.5782	.645	.593	.720	6.16
.80	.924	8.23	.6652	.720	.630	.699	6.34
.85	.948	8.91	.7530	.795	.664	.679	6.53
.90	.968	9.59	.8394	.867	.692	.662	6.72
.95	.985	10.25	.9226	.936	.717	.647	6.91
1.00	1.000	10.87	1.0000	1.000	.737	.634	7.08

Table 3, taking as argument the ultimate distances from the center of what were the surface particles at the respective epochs, shows the variation of the relative radius, central density, mass, and surface gravity, of the growing planet, together with the depression factor for differential accretion, and the factors used in determining the effect of differential accretion on the moment of inertia; in every case in terms of  $\beta_s$ , which represents the actual momentary radius.

TABLE 4.

<u>βε</u> β <sub>1</sub>	e₁ ∞ 10—•	<u> 5e, w</u>	V∞ <del>mi</del>	s
0.00	0.0	0	0.00	1.000
.05	1.9	230	.39	.998
.10	7.7	920	.77	.993
.15	17.4	2,070	1.16	.986
.20	30.9	3,680	1.55	.976
.25	48.3	5,750	1.93	.963
.30	69.4	8,260	2.31	.948
.35	94.2	11,210	2.70	.931
.40	122.5	14,590	3.08	.914
.45	154.4	18,380	3.45	.896
.50	189.5	22,560	3.83	.877
.55	227.7	27,110	4.19	.861
.60	268.6	31,980	4.55	.846
.65	311.9	37,130	4.91	.834
.70	356.9	42,490	5.25	.826
.75	403.2	48,000	5.58	.824
.80	450.1	53,560	5.90	.830
.85	496.6	59,120	6.19	.845
.90	541.9	64,510	6.47	.874
.95	585.0	69,640	6.72	.923
1.00	624.9	74,390	6.95	1.000

Table 4 is a continuation of table 3, giving in terms of the same argument the specific energy of impact for a particle falling from infinity, in billions of ergs per gram, the same in centigrade degrees under specific heat 0.2, the surface parabolic velocity in miles per second, and the distortion factor indicating the permanent deformation of elements of the mass at the various points along the radius.

#### THE THERMAL PROBLEM.

It has been supposed in the foregoing that the distribution of heat was not sensibly affected by conduction during the relatively short epoch of accretion. If, now, it be supposed that the subsequent changes in distribution are determined by conduction only, in accordance with Fourier's laws, then the form of the temperature curve  $\theta = \theta(r,t)$  at each instant may be determined by the differential equation

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( \lambda r^2 \frac{\partial \theta}{\partial r} \right) = \sigma \rho \frac{\partial \theta}{\partial t} \tag{52}$$

provided the form of the curve at the initial instant, say t=0, appropriate conditions relating to the surface, and the values of the conductivity  $\lambda$  and specific heat  $\sigma$  be assigned. Since the variations of  $\lambda$  and  $\sigma$  under changes in the physical condition of the substance are almost purely matters of conjecture, the chief value of such an inquiry might well be considered to lie in the determination of features of the thermal phenomenon which seem to persist under varied assumptions on these points. Since, however, the method of superposition of special solutions is practically the only known way of obtaining general solutions of equations like (52), it will be supposed that the latter is linear,  $\lambda$  and  $\sigma$  being assigned in each special case as functions of r but independent of  $\theta$ , and that the surface equations are linear and homogeneous in  $\theta$  and its derivatives.

According to Fourier's method, of expansion into an infinite series each term of which is a solution of (52) and satisfies the surface condition, the solution may then be sought in the form

$$\theta(r,t) = \sum_{n=1}^{n=\infty} A_n e^{-\frac{t}{r_n}} y_n(x)$$
 (53)

where

$$\tau_n = \frac{\sigma_0 \rho_0 r_1^2}{\lambda_0 \mu_n} \tag{54}$$

and  $y_n$  (x) or y ( $\mu_n$ , x) for n=1 . . .  $\infty$  are the appropriate fundamental functions, which are to be determined from

$$\frac{1}{x^2} \frac{d}{dx} \left( x^2 \psi(x) \frac{dy}{dx} \right) + \mu \varphi(x) y = 0 \qquad y_{x=0} = 1 \qquad \frac{dy}{dx} \Big|_{x=0} = 0 \quad (55)$$

where  $\psi(x) = \lambda/\lambda_0$ ,  $\varphi(x) = \sigma\rho/\sigma_0\rho_0$ , and the successive values of  $\mu$  employed are those which allow the individual terms of (53) to satisfy the surface condition. The coefficients in (53) will be given by

$$A_{n} = \theta_{0} \frac{\int_{0}^{1} x^{2} \varphi(x) F(x) y_{n}(x) dx}{\int_{0}^{1} x^{2} \varphi(x) \overline{y_{n}(x)^{2}} dx}$$
 (56)

if the primitive temperature curve is given in the form

$$\theta(r,0) = \theta_0 F(x) \tag{57}$$

 $\theta_a$  being the initial temperature at the center.

To determine the form of this initial curve it is necessary to know in what way the storage of the compressional and impact energy is manifested in rise of temperature, which is again a matter of hypothesis. Fisher's third assumption, as stated above, implies that the energy stored in unit-mass stands in a definite ratio to the increment of temperature. That ratio is, then, of the nature of a specific heat, expressed in mechanical units, but is subject to question as to its identification, as is tacitly done by Fisher, with the specific heat in the ordinary sense, as relating to rise of temperature due to heat transferred by conduction or radiation. It will be shown later, however, in connection with a detailed criticism, that the theory thus developed may fairly be considered self-consistent, in the light of thermodynamic laws, when associated with what appears as a certain extreme view regarding the thermodynamic properties of the earth-substance. An effort will then be made to develop an opposite extreme view, to permit comparison.

For the present, then, the primitive temperature will be supposed defined by

$$\theta = \frac{e + \nu e_i}{\sigma J} \tag{58}$$

where  $\nu$  is the fractional value of that part of the energy of impact which remains after the loss by dissipation at the surface, and  $\sigma$  is the specific heat identical with that occurring in equation (52). A variation of  $\sigma$  with the density need not be excluded, but any possible variation with the temperature will be disregarded, not only because of the practical value of keeping the linearity of equation (52), but also because any uncertainty from this source would be bound up with the inevitable obscurity of the very notion of temperature under circumstances so far beyond the range of laboratory tests.

The multiplier  $\nu$  may also vary for different portions of the mass, its value depending on the rapidity of the accretion. It could be unity as one extreme, for deposits made with such rapidity that each stratum is covered up before its loss of heat by radiation is sensible; or zero as the other extreme, for accretion so slow that the cooling of the momentary surface-stratum by radiation is practically complete.

One curious possibility may be noted in passing. With sufficient velocities of impact and appropriate values of  $\nu$ , it would be possible for the expression  $e + \nu e_i$  to have the same value for all strata; if then  $\sigma$  were likewise constant, this would indicate a primitive temperature uniform throughout the body. For example, if  $e_i$  should be for each stratum that derived from impact at the corresponding parabolic velocity, as listed in table 4, and  $\nu$  should range from 0.38 for the central portions to 0.27 for the surface layer, then  $e + \nu e_i$  would have everywhere the value  $1.7 \times 10^{11}$  ergs per gram mass, and for  $\sigma = 0.2$  this would give a primitive temperature of about 20,000°. Since this value of  $\sigma$  may be too low, and it is practically certain

that not all of the energy can be considered as manifested in the raising of the temperature, this number is probably somewhat too high. But in any case it appears that the planetesimal hypothesis could thus plausibly assign an origin for precisely the kind of initial thermal condition of the mass postulated in Kelvin's famous theory, which would then serve to indicate the subsequent thermal process, and in particular the probable age of the earth reckoned from the close of the epoch of formation.

It seems, however, more in accord with the spirit of the general hypothesis to assign no such relative importance to the energy of impact. For the value of  $e_i$  should probably be assumed much less than its parabolic value, being due to the relative velocities simply of bodies which might partake more or less of a common motion; for instance of bodies moving in similar directions around the sun in intersecting orbits of moderate eccentricity. Moreover, even with what might be considered a rapid rate of accretion, when compared with astronomical processes in general, by far the greater part of the heat so generated must be expected to escape quickly by radiation, thus making  $\nu$  a small fraction. The computations following refer to the case when the value of  $\nu e_i$  is insignificant, so that the compressional energy alone is effective in producing the primitive temperatures, which are then to be computed from column 6 of table 2 and the assumed values of  $\sigma$ .

The same relative freedom of dissipation into space would tend to keep the surface at a low and equable temperature after the accretion had ceased. It will, therefore, be assumed that the surface temperature keeps a fixed value, which may be taken as the zero of reckoning, and whose place in an absolute scale would depend largely on the thermal influence of the atmosphere. It is further supposed that the rise of temperature produced by compression can be reckoned from this point. With these stipulations the solution will be determined if definite hypothesis is made regarding the conductivity and specific heat.

If  $\lambda$  and  $\sigma$  are uniform throughout the mass, then  $\psi(x) = 1$ , and  $\varphi(x) = \rho/\rho_0$ . Since great precision is needless in these computations, the ratio  $\rho/\rho_0$  will be replaced by the convenient expression  $(1-\frac{1}{2}x^2)^2$ , whose close accordance with it appears from columns 4 and 5 of table 1, and which simplifies the determination of the solutions of equation (55), which then reduces to

$$\frac{1}{x^2} \frac{d}{dx} \left( x^2 \frac{dy}{dx} \right) + \mu \left( 1 - \frac{1}{2} x^2 \right)^2 y = 0$$
 (59)

the required solution of which may be written:

$$y(\mu, x) = \sum_{i=0}^{i=\infty} (-1)^{i} a_{i} x^{2i}$$
 (60)

where the a's, which are functions of  $\mu$ , are all positive and determined by the simple recursion-formula

$$a_{i} = \frac{\mu}{2i(2i+1)}(a_{i-1} + a_{i-2} + \frac{1}{4}a_{i-3}) \qquad a_{0} = 1 \qquad a_{i} = \frac{\mu}{6}$$
 (61)

The values of  $\mu$  required for the expansion (53), with the surface condition named, are the roots, infinite in number, of the equation

$$y(\mu, 1) = \sum_{i=0}^{i=\infty} (-1)^{i} a_{i} = 0$$
 (62)

These roots may be determined as far as required by a trial and error tabulation of  $y(\mu, 1)$ , the computation yielding also the coefficients  $a_{\nu}$  but increasing rapidly in length with each succeeding root. The first two roots and the corresponding fundamental functions are:

$$\mu_1 = 13.0589$$

$$y_1(x) = 1 - 2.17648 x^2 + 2.07407 x^4 - 1.39934 x^6 + .72867 x^8 - .31419 x^{10} + .11658 x^{12} - .03812 x^{14} + .01120 x^{16} - .00300 x^{18} + .00074 x^{20} - .00017 x^{22} + .00004 x^{24} - .00001 x^{26} \cdot . \cdot . \cdot$$

$$\mu_2 = 55.313$$

$$y_2(x) = 1 - 9.21889 x^2 + 28.26204 x^4 - 49.69103 x^6 + 61.65731 x^8 - 59.54423 x^{10} + 47.37952 x^{12} - 32.22346 x^{14} + 19.21509 x^{16} - 10.23514 x^{18} + 4.93949 x^{20} - 2.18394 x^{22} + .89259 x^{24} - .33971 x^{20} + .12114 x^{26} - .04068 x^{20} + .01292 x^{22} - .00390 x^{64} + .00112 x^{26} - .00031 x^{38} + .00008 x^{46} - .00002 x^{42} \cdot . \cdot \cdot$$

The number of terms to be included and the magnitude of the individual coefficients increase rapidly with the index of the component, so that if many components are of sensible influence in the representation of the primitive temperature curve, the accurate determination by this method of the transformations produced by conduction would require computations of serious length. But the effect of the higher components on the general features of the cooling process can be conjectured, with the aid of certain general properties of the fundamental functions which are obvious in the light of the theory of linear differential equations of the second order.

The constants  $\mu_1$ ,  $\mu_2$  . . . will show a rough proportionality to the squares of the natural numbers. The solutions  $y(\mu_n, x)$  or  $y_n(x)$  will be oscillatory in such wise that  $y_n$  has n-1 roots between 0 and 1, the intermediate half-waves having amplitudes all less than the central amplitude, which is unity, and decreasing in order when counted from x=0 toward x=1, exhibiting these features in a more marked fashion than the functions  $\frac{\sin n\pi x}{n\pi x}$ , because of the fact that the coefficient  $\varphi(x)$  decreases as x goes from 0 to 1.

For constant  $\sigma$  the primitive temperature curve is obtained from the curve for  $e/e_0$ , which has unit amplitude at the center, by multiplying all ordinates by the central temperature,  $\frac{e_0}{\sigma J}$ ; which for  $\sigma = 0.2$  is about 20,000°, the temperatures being then given by column 8 of table 2.1 It

¹ The temperatures given by Fisher are larger than those here listed in the ratio of the number of pounds in a cubic foot of water, presumably through some inconsistency in the units used in the equivalents of formulas (21) and (22), which however does not occur in the corresponding expressions in his "Physics of the Earth's Crust," p. 29.

will be convenient however to express the temperatures and coefficients  $A_i$  in terms of the central temperature as unit, to leave free choice as to the numerical value of  $\sigma$ . The coefficients  $A_1$ ,  $A_2$  then have the values named below, computed according to (56) by mechanical quadrature.

The influence of the first two components appears from table 5. The second and third columns give the first two fundamental functions, the fourth the primitive temperature curve, and the next two the terms outstanding after subtraction of the first and of the first two components respectively.

TABLE 5.

x	<b>y</b> 1	V2	F(x)	$F_1(x)$	$F_2(x)$	· 30 .
0.00	1.0000	1.0000	1.0000	-0.0537	-0.0372	-10.00
.05	.9946	.9771	.9957	0523	0362	9.97
.10	.9784	.9106	.9830	0480	0330	<b>— 9.89</b>
.15	.9521	.8063	.9619	<b>— .0413</b>	0280	9.76
.20	.9162	.6734	.9329	<b>— .0325</b>	0214	<b>— 9.57</b>
.25	.8717	.5230	.8961	0225	0139	<b>— 9.33</b>
.30	.8199	.3667	.8520	0120	0059	9.03
.35	.7621	.2158	.8011	0019	+ .0017	8.67
.40	.6996	.0798	.7441	+ .0070	→ .0083	8.24
.45	.6338	0343	.6814	+ .0135	+ .0129	7.74
.50	.5662	1222	.6141	+ .0175	+ .0155	<b>— 7.16</b>
.55	.4981	<b>— .1826</b>	.5434	+ .0186	+ .0156	- 6.50
.60	.4305	2164	.4697	i → .0160	→ .0124	5.73
.65	.3647	2266	.3945	+ .0102	+ .0065	4.82
.70	.3024	2175	.3191	+ .0005	0031	3.76
.75	.2414	<b>—</b> .1937	.2452	0092	0124	- 2.47
.80	.1849	1599	.1749	<b>—</b> .0199	0225	0.86
.85	.1325	1205	.1105	0291	0311	+ 1.21
.90	.0842	0790	.0559	0328	0341	+ 4.01
.95	.0401	0382	.0162	0260	0266	+ 8.02
1.00	.0000	.0000	.0000	.0000	.0000	+14.22

Here

$$F_1(x) = \theta/\theta_0$$
, the primitive temperature curve;  $F_1(x) = F_1(x) - A_1y_1(x)$   $A_1 = 1.0537$   $F_2(x) = F_1(x) - A_2y_2(x)$   $A_2 = -0.0165$ 

In the seventh column  $\frac{\partial \theta}{\partial t}$  is the initial rate of change of temperature in convenient units according to equation (65) below; these entries, to be reduced to absolute units, must be multiplied by  $\frac{\theta_0 \lambda_0}{\sigma_0 \rho_0 r_1^2}$ ; as they stand the unit of change would be about  $3\frac{1}{2}$ ° in a billion years, with the numerical constants used.

The results show that the first component is by far the most important; its amplitude at the center differs from that of the temperature curve by only  $5\frac{1}{3}$  per cent, and the divergences fall below that percentage over a range of more than eight-tenths of the radius from the center. If this component alone were present the temperature at any time would be represented by

$$\theta = A_1 e^{-\frac{t}{\tau_1}} y_1(x)$$

exhibiting the simple type of cooling described by Fourier, where conduction produces simply a progressive diminution in the ordinate scale of the temperature curve, according to the time-exponential law, without change in the ratios of the ordinates. Since  $y_1(x)$  is everywhere positive, this would mean an actual decline of temperature at each point proportional to the temperature itself. The gradient at the surface would be initially 1° in 417.5 meters, for  $\sigma$ =0.2, and would decline according to the same law as the temperatures themselves. This shows that under the condition for the moment assumed only a small part of the present observed gradient, about 1° in 30 meters, could be ascribed to this component, unless the specific heat were taken very low.

The time-rate of the process is specified conveniently by means of the interval  $\tau$ , which is the time required to reduce the amplitude of the corresponding component to  $\frac{1}{e}$  or 0.368 of its primitive value, and is to be determined by (54), when the value of  $\frac{\lambda}{\sigma\rho}$ , the "thermometric" conductivity, is assigned. If the latter be taken in the neighborhood of 0.01 for surface rock, the value of  $\frac{\lambda_0}{\sigma_0\rho_0}$  being one-fourth of this, the value of  $\tau_1$  is about  $4\times10^{11}$  years. The time required to reduce the amplitude of the first component by 1 per cent would be about four billion years.

Any higher component dies out in a similar way, at a rate indicated by its value of  $\tau$ ; but because of the alternation in sign of the fundamental function, would, if occurring singly, indicate falling and rising of temperature for successive zones in alternate order along the radius, the number of zones being equal to the index of the component, with the central temperature falling or rising according to the positive or negative sign of the coefficient A. Thus the second component has a negative coefficient, in magnitude less than one-sixtieth that of the first, but with  $\tau_2$  somewhat less than  $\frac{1}{4}\tau_1$ ; since  $y_2$  is everywhere numerically less than  $y_1$ , this means that with respect to changes of temperature the second component simply modifies the effect of the first nowhere to an extent more than one-fifteenth of the total effect due to the latter alone. In the zone extending 0.43 of the radius from the center the temperature falls somewhat more slowly and thence outwards more rapidly with only these two components included than would be the case with the first alone.

The influence of each further component could be traced in a similar way, and many would doubtless be found to be sensible within the range of accuracy of the tables above, if the computation to that degree of accuracy should prove to be feasible. But in the absence of simple analytic expressions for the functions involved it would be necessary to do this by numerical calculations of extreme length on account of the greater and greater number of the coefficients  $a_i$  needed, and the insufficiency for determining the coefficients  $A_i$  of a tabulation of the functions with a moderate number of entries.

The residuals in column 6 show that the influence of the higher components is meager in the central portions, but relatively serious in the more

superficial zones. It is accordingly in the latter region that such general considerations as above are insufficient to give a just idea of the complete thermal process.

Conjecture may, however, be made with some confidence as to the probable character of the modifications produced by the higher components, by direct inspection of the primitive temperature curve, which by (22) and (58), with the substitution of the approximate expression used previously for the density, becomes

$$\theta = \theta_0 (1 - x^2)^2 (1 - \frac{1}{3} x^2)^2 (1 - \frac{1}{2} x^2)^{-2}$$
 (64)

which is accurate enough for the purpose. Then, according to (52), the initial rate of change of temperature becomes:

$$\frac{\partial \theta}{\partial t} = \frac{\theta_0 \lambda_0}{\sigma_0 \rho_0 r_1^2} \left\{ -10 + \frac{275}{9} x^2 - \frac{304}{9} x^4 + \frac{56}{3} x^6 - \frac{46}{9} x^8 + \frac{5}{9} x^{10} \right\} \div \left\{ 1 - \frac{1}{2} x^2 \right\}^4$$
 (65)

in which the coefficient of  $\frac{\theta_0\lambda_0}{\sigma_0\rho_0r_1^2}$  is that tabulated in column 7 of table 5. For the part of  $\frac{\partial\theta}{\partial t}$  due to any single component, say the *n*th, the corresponding coefficient would be  $\mu_nA_ny_n$ .

These figures indicate that from the center outwards over a distance of about eight-tenths of the radius the thermal process is not very different from that represented by the first component alone, except that the latter exaggerates the rate of decline somewhat in the more central portions on account of the opposing effect of the higher components. But in the outer zone of about two-tenths of the radius the process is in the earlier stages totally different; here the temperature actually rises for a certain interval of time, which would be different for different depths, very short for points extremely near the surface because of the constancy of the surface-temperature, and for points near the boundary between the regions of rising and of falling temperature, but presumably of considerable length at intermediate depths. Since this trend of temperature in the outer zone is brought about by the higher components, which practically die out in a time sufficient to produce only a relatively small change in the amplitude of the first component, the whole process may be conceived to occur in two epochs, an earlier one of gradual accommodation of the temperature-curve to the slowly declining first component, and a later one where that component is left practically isolated. During the latter epoch the temperature would decline steadily at all points at rates nearly proportional to the existing temperatures. But during a large part of the earlier epoch the heat lost from the central portions is conducted through an intermediate zone, whose thermal condition is nearly stationary, and thence outwards to produce an exaltation of temperature in a zone a few hundred miles thick just below the surface. Dissipation through the surface in the earlier stages is very slight, owing to the smallness of the gradient, the primitive temperature-curve being tangent to the x-axis at the point x=1, because of the occurrence of the squared factor  $(\rho - \rho_1)^2$  in formula (22).

The zone of rising temperature, which would be narrowed down and finally disappear as the conduction progressed, extends at the start from the surface to a depth of about 700 miles. The total rise of temperature would be trivial near the extremes of this zone, but more marked toward its interior. According to the residuals in column 6, table 5, the rise may be expected to be most significant in the neighborhood of a depth of about 400 miles, reaching in that region, with allowance for even a considerable percentage of decline in the first component, a value of probably at least two one-hundredths of the central temperature, or 400°, which is the increase over initial temperatures ranging about 1,200°. Such a change might carry the substance through its temperature of fusion, even under the high pressures there sustained.

The foregoing sketch of the thermal process lacks, of course, the precision which could be reached through a computation extended to include all components of sensible influence; this also would alone suffice to yield an accurate estimate of the time-intervals implied, which would probably be counted in billions of years for the epoch during which rising temperatures occur. It must be noted also that a small outstanding portion of the energy of impact might alter the features of the thermal process seriously, especially in the strata near the surface, where the very fact of the occurrence of the rising temperatures may be said to be due to that relative deficiency in the heat from the purely compressional source which is represented by the upward concavity of the initial temperature-curve.

It is desirable, however, to know more precisely the result of the complete computation, under at least one set of reasonable assumptions, which, in the absence of experimental information, may fairly be conditioned by the practicability of the calculations; for instance, through the use of a suitable alternative hypothesis regarding the specific heat. This has thus far been treated as a constant, but there would seem to be some reason, under a molecular theory, for supposing it to decrease with increase of density, since the consequent diminution of the intermolecular spaces might tend to throw more of the energy into the "unordered" kinetic or thermal form, by interfering with the "ordered" movements which have been conceived by Hertz and others to account for the storage of energy apparently in latent or potential form. It will be of interest to see how far the thermal process described above is modified by supposing the specific heat thus variable.

A simple supposition on this point, hardly more arbitrary than any other that could be made and having at least the merit of yielding tractable formulas, is that  $\sigma$  is inversely proportional to  $\rho$ , or  $\sigma\rho = \sigma_1\rho_1$ . With constant "calorimetric" conductivity  $\lambda$  this makes the "thermometric" conductivity

 $\frac{\lambda}{\sigma o}$  also constant, and reduces equation (55) to the form:

$$\frac{1}{x^2}\frac{d}{dx}\left(x^2\frac{dy}{dx}\right) + \mu y = 0 \tag{66}$$

giving for the fundamental functions:

$$y_n = \frac{\sin n\pi x}{n\pi x} \tag{67}$$

and for the expansion (53) the coefficients:

$$A_n = 2n\pi \int_a^1 x F(x) \sin n\pi x \, dx \tag{68}$$

if the initial temperature-curve is  $y = \theta_0 F(x)$  and the coefficients are expressed in terms of  $\theta_0$  as unit. The intervals  $\tau$  are determined by

$$\tau_n = \frac{\sigma_1 \rho_1 r_1^2}{\lambda n^2 \pi^2} \tag{69}$$

and are thus in this case strictly proportional to the squared reciprocals of the natural numbers.

To determine F(x), it may be noted that the initial temperatures can be determined from those of the previous hypothesis by multiplying by  $\rho|\rho_1$ ; giving for the central temperature

$$\theta_0 = \frac{h}{2J\rho_1\sigma_1}(\rho_0 - \rho_1)^2 \tag{70}$$

which for  $\sigma = 0.2$  is about 81,000°; and for the curve in terms of the central ordinate

$$\frac{\theta}{\theta_0} = F(x) = \left(\frac{\rho - \rho_1}{\rho_0 - \rho_1}\right)^2 \tag{71}$$

For convenience in determining the coefficients  $A_n$  the last equation will be replaced by the formula

$$F(x) = (1-x^2)^2(1-\frac{5}{7}x^2+\frac{1}{5}x^4)$$

or

$$F(x) = 1 - \frac{19}{7}x^2 + \frac{92}{35}x^4 - \frac{39}{35}x^6 + \frac{1}{5}x^8$$
 (72)

which, in comparison with (71), leaves residuals at most 3 units in the fourth decimal place. By (68) the expansion has then the coefficients

$$A_{\rm n} = 2n \left\{ \frac{1}{\pi} S_{\rm n}{}^{\scriptscriptstyle (1)} - \frac{19}{7\pi^{\rm 3}} S_{\rm n}{}^{\scriptscriptstyle (2)} + \frac{92}{35\pi^{\rm 5}} S_{\rm n}{}^{\scriptscriptstyle (3)} - \frac{39}{35\pi^{\rm 7}} S_{\rm n}{}^{\scriptscriptstyle (4)} + \frac{1}{5\pi^{\rm 9}} S_{\rm n}{}^{\scriptscriptstyle (5)} \right\}$$

where

$$S_n^{(\kappa)} = \int_0^{\pi} \varphi^{2\kappa - 1} \sin n\varphi \, d\varphi$$

which can be reduced through integration by parts, giving finally

$$A_n = 2 (-1)^{n-1} \left\{ -\frac{136}{35n^2\pi^2} - \frac{552}{35n^4\pi^4} - \frac{6480}{n^6\pi^6} + \frac{72576}{n^6\pi^6} \right\}$$
 (73)

The first few of these coefficients are:

$$A_1 = +0.70590$$
  $A_2 = +0.36797$   $A_4 = +0.05354$   $A_6 = +0.02240$   $A_3 = -0.10765$   $A_5 = -0.03284$   $A_7 = -0.01632$ 

The alternation of the sign begins with the second and the steady decline in numerical value continues throughout.

A convenient unit of time for exhibiting the changes produced by conduction in the temperature-curve is the interval T required to reduce the amplitude of the first component by 1 per cent, which with the same constants as before, for the surface-stratum, would be about  $1\frac{1}{3}$  billion years. The successive changes in the temperature-curve are shown in table 6, abbreviated from an extended computation covering an epoch of 35 such intervals, the number of terms of the series included ranging from 100 for the earliest entries to 5 for the latest. The unit of temperature is the initial temperature at the center.

TABLE 6.

z	<b>0</b> (0)	● (5T)	• (10 <i>T</i> )	● (15T)	● (20T)	● (25T)	# (80 T)	# (85T)
0.00	1.0000	0.9210	0.8496	0.7849	0.7263	0.6734	0.6256	0.5823
.05	.9932	.9149	.8440	.7798	.7218	.6693	.6219	.5790
.10	.9731	.8967	.8275	.7649	.7083	.6571	.6109	.5690
.15	.9402	.8669	.8006	.7406	.6863	.6372	.5928	.5527
.20	.8956	.8265	.7640	.7075	.6564	.6101	.5683	.5305
.25	.8404	.7765	.7188	.6666	.6194	.5767	.5381	.5031
.30	.7762	.7185	.6663	.6191	.5765	.5379	.5030	.4712
.35	.7049	.6540	.6080	.5664	.5288	.4948	.4639	.4357
.40	.6286	.5849	.5456	.5100	.4778	.4486	.4220	.3976
.45	.5492	.5132	.4808	.4514	.4248	.4006	.3783	.3577
.50	.4691	.4408	.4153	.8923	.3713	.3519	.3339	.3171
.55	.3903	.3697	.3511	.3341	.3185	.3038	.2899	.2766
.60	.3149	.3016	.2896	.2784	.2677	.2573	.2471	.2370
.65	.2447	.2383	.2323	.2263	.2200	.2133	.2062	.1990
.70	.1816	.1812	.1806	.1789	.1761	.1724	.1680	.1630
.75	.1266	.1316	.1352	.1368	.1366	.1351	.1326	.1294
.80	.0810	.0903	.0966	.1001	.1015	.1015	.1003	.0985
.85	.0453	.0574	.0648	.0688	.0708	.0715	.0712	.0702
.90	.0200	.0326	.0389	.0423	.0441	.0449	.0449	.0445
.95	.0049	.0143	.0178	.0197	.0207	.0212	.0213	.0211
1.00	0	0	0	0	0	0	0	0

Here, as in the previous case, the earlier stages of the conduction are marked by the division of the mass into two zones, an inner where the temperature falls and an outer where it rises. The spherical surface of boundary between these lies initially at a depth of not quite 1,200 miles, and as the conduction progresses rises toward the surface. Its passage through any particular horizon marks the attainment of the maximum temperature which occurs at that depth; while its ultimate coalescence with the free surface, simultaneous with the occurrence of the maximum surface gradient, indicates the final establishment of a downward trend of temperature throughout the body. This decline during the further progress of the conduction is in the outer portions first accelerated and later retarded, and is ultimately everywhere of a character more and more closely approximating to the simple type represented by the first component alone.

Table 7 gives numerical data, with the epochs reckoned from the beginning of the conduction:

TABLE 7.

z	Depth in miles.	Epoch of maximum temperature.	Initial temperature.	Total rise.
0.75	1000	16.9 T	10,240°	830°
.80	800	22.2 T	6,550	1,680
.85	600	25.6 T	3,660	2,130
.90	400	27.8 T	1,620	2,020
.95	200	29.1 T	400	1,330

The zone of rising temperatures vanishes at epoch 29.7 T, corresponding to the maximum surface gradient of 1° in about 180 meters, about one-sixth of that obtained from observations at the present time. The greatest total rise of temperature occurs at depth about 480 miles, where it is 2,200°, with initial temperature 2,340°.

As compared with the former case sketched above, the results of the present assumptions, though giving considerably larger primitive temperatures, show a close qualitative similarity in the thermal changes. But the zone of rising temperatures is at first somewhat deeper, the temperatureincrements within it are greater, and the period of its existence longer. This is to be ascribed largely to the influence of the second component of the series, whose coefficient is here large, while in the former case it is relatively trivial. In both cases the conductivity has been treated as constant. It has often been supposed, however, that it would probably increase considerably with increase of density. The effect of this would be to facilitate the transfer of heat from the central parts to the outer zone, presumably increasing the total temperature-increments there, perhaps shortening the time during which the temperature rises. It would be likely, also, to increase the value of the maximum surface-gradient, but whether this could be brought up to the present observed value through any reasonable assumption of this character remains to be determined.

The magnitude of the thermal changes in the zone of rising temperatures, resulting from the arbitrary special conditions developed above, seems to make it probable that the existence of this zone should be considered an essential feature of the thermal process under the planetesimal hypothesis.

## PART II.—CRITICAL AND SUPPLEMENTARY.

In the development of the theory in Part I, the attempt was made to give explicit statement, though without critical setting, of the more important of the secondary hypotheses which were used as auxiliary to the general hypothesis in order to give the theory a sufficiently definite form. But since the main purpose is to seek such features of the geophysical phenomena as seem to be essentially consequences of the general hypothesis, it is necessary further to inquire how far the results are peculiar to the special conditions adopted and how far they seem to persist under variations of these secondary assumptions; and also to what extent these assumptions are subject to obscurity or positive objection through the accessibility of a direct or indirect test by observation or well-established theory.

The Laplacian law of density has been assumed chiefly because of its analytic convenience, though it seems doubtful whether any geophysical theory is likely to be sufficiently trustworthy in detail to afford more than a crude test of any assumption on this point. Nevertheless, by inspection of some of its consequences, it is possible to surmise the probable character of its departure from the true law of compressibility of the average earth-substance. It appears that the modifications which seem to be needed from the standpoint of the planetesimal hypothesis agree, at least in kind, with those familiar from the indications of general geophysical theory.

Column 7 of table 3 shows that in the earlier stages of the growth of the planet the thickness of a stratum deposited is nearly all effective in enlarging the geometric radius of the mass, while toward the last not much more than one-quarter of a new stratum remains above the former horizon; as the mass grows larger the less significant becomes the actual increase of dimensions produced by a new stratum of given thickness. Moreover, with a strict interpretation of the law of compressibility assumed above, there is a definite limit to the possible radius of the planet, no matter how much material might be laid down. For in equation (25) the factor q is a definite constant, depending solely on h, which is determined by the compressibility as a physical constant of the material, independent of the dimensions of the mass into which it may be aggregated; while if there are to be no meaningless negative densities introduced, the angle  $\beta$  can not surpass the This means value  $\pi$ , at which the density at the center becomes infinite. that no amount of accretion could produce a mass with radius greater than  $\frac{\pi}{}$  centimeters, or about 5,000 miles.

Now, even independently of any supposition as to the actual origin of the planets, there seems to be little reason for supposing that if deposits of indefinite extent could be brought about at the surface of an existing planet there would be such a limit of growth, at least of such comparatively meager dimensions. This objection has not much force, for the reason that the law might be practically accurate for the range of densities contemplated and seriously in error for the higher densities; but its suggestion is that the true

compressibility most probably diminishes, as the density increases, more rapidly than is postulated by the Laplacian law. This would allow a larger part of the compression to take place during the earlier stages, giving to the nucleus, when it reaches a given radius, a larger mass than is assigned it above.

In the light of the planetesimal hypothesis a similar conclusion can be reached in another way. For in view of the like origin predicated of the earth and other bodies of the solar system from the primitive planetesimals, composed of more or less similar materials of definite compressibility, it may be expected that at the successive stages when the earth-nucleus reached dimensions equal to those of various planets at the present time its mass should show some agreement with the observed masses of those planets. The supposition of the small upper limit of diameter just mentioned is of course negatived by the existence of the planets of the Jovian group. But such comparison is futile, partly because of the uncertainty as to their true dimensions, brought about by their extensive atmospheres, partly because of the wide difference in physical condition as compared with the earth, illustrated in particular by mean densities smaller than even the surface-density assumed for the earth. Moreover, it is conceivable that the discrepancies of an assumed pressure-density law might become serious only outside of the range met with in smaller bodies like the earth. But a comparison with the other planets of the terrestrial group should prove instructive. Table 8 gives their observed radii and masses as compared with the earth, and the hypothetical masses computed by interpolation from columns 2 and 4 of table 3.

TABLE 8.

	Relative radius.	m observed.	computed.
Moon	0.273	0.0121	0.0103
	.382	(?)	.029
	.534	.107	.086
	.972	.78	.85

To interpret this table it is necessary to observe that if the masses corresponding to assigned dimensions be computed according to two different laws of compressibility, using the mean and surface-densities of the present earth as given constants, then those masses must approach agreement, on the one hand for small bodies where the compression is slight and the average density therefore not very different from the assigned surface-density, on the other hand for bodies approximating the earth in size, the average density then approaching the assigned mean density. Thus it appears that the divergence of result between two such assumptions would be likely to be most marked for bodies of intermediate size, like Mars, Mercury, and the moon, while the agreement should be close for Venus on the one hand and the asteroids on the other—as, for instance, if the masses resulting from the Laplacian law be compared as above with the observed masses, supposing the latter to correspond to a definite, though unknown, law of compressibility.

The masses of the asteroids are purely conjectural, while that of Mercury is too uncertain to be used. For Venus the computed mass exceeds the observed; but at least part of the difference may be ascribed to the influence of atmosphere and irradiation in bringing about an overestimate of the planet's true diameter; for example, if the observed radius were corrected by -2 per cent of its value, the computed and observed masses would agree. For the moon and Mars, the computed masses fall below the observed by 15 per cent and 20 per cent, respectively.

From this, as before, the suggestion is that the assumed law of compression should be modified in the direction of allowing greater compressibility at the lower densities, and less at the higher, which would have the effect of assigning greater mass to the nucleus at intermediate sizes, and to the present earth a steeper density-gradient near the surface, together with a relatively more nearly homogeneous central portion. This agrees with conclusions which have been drawn from observations of precession and the transmission of seismic disturbances.

In view of this comparison it seems quite conceivable that a law of compressibility might be constructed, agreeing with the data furnished by the earth in its present condition, and such that the observed masses of the planets now existing in its neighborhood would prove to be the same as those computed for the nucleus at epochs when the dimensions correspond. It will accordingly be of interest to review the previous theory, with the substitution of a density-formula whose variations from that of Laplace have the general trend indicated.

A formula of this character for the density is the simple one proposed by Roche:  $\rho = \rho_0 (1 - cx^2)$  c = const. (74)

From this, according to the general equations previously used, are derived:

$$m = \frac{4}{3} \pi \rho_0 r^2 \left( 1 - \frac{3}{5} c x^2 \right) \tag{75}$$

$$\frac{dp}{d\rho} = \frac{4\pi k \,\rho_0 \,r_1^2}{15c} \left(z + \frac{3}{2} \,z^2\right) \tag{76}$$

whence H is determined by (15); also:

$$p = \frac{A}{c} \left\{ (z^2 - z_1^2) + (z^3 - z_1^3) \right\}$$
 (77)

$$e = \frac{A}{2\rho_0 c} (z - z_1)^2 \cdot \frac{z + 2z_1 + 2}{z}$$
 (78)

$$\rho_{m} = \rho_{0} \left( 1 - \frac{3}{5} c \right) \qquad \rho_{1} = \rho_{0} \left( 1 - c \right) \tag{79}$$

$$E = 8\pi A r_1^{s} \cdot \frac{2}{21} c \left( 1 - \frac{7}{15} c \right)$$
 (80)

$$\mathbf{0} = 8\pi A r_1^2 \left( 1 - \frac{8}{7} c + \frac{1}{3} c^2 \right) \tag{81}$$

<sup>&</sup>lt;sup>1</sup> Roche, Académie des Sciences et Lettres de Montpellier, v. 8, 1848, p. 235.

in which are put

$$A = \frac{2}{15} \pi k \rho_0^2 r_1^2 \qquad s = \frac{\rho}{\rho_0} \qquad z_1 = 1 - \epsilon$$

The constants  $\rho_0$ , c may be determined by assigned values of the mean and surface densities, which will here be supposed to be in the ratio 2:1, giving  $c = \frac{5}{7}$ , whence results

$$ho_0 = 9.653$$
  $ho_1 = 2.758$   $H_1 = 3.45 \times 10^{11}$   $E = 3.110 \times 10^{38}$   $\theta = 2.426 \times 10^{38}$ 

and for the quantities  $\rho$ , p, H at various depths the values listed in table 9, which for the present density-formula replaces the corresponding columns in tables 1 and 2. This value of c is somewhat less than that used by Roche, which seems to give rather too small an estimate for the surface-density, when the more modern determinations of  $\rho$ , are used.

when the more modern determinations of  $\rho_m$  are used.

Comparison with the tables of Part I shows that the range of values in density, pressure, and specific compressional energy is in each case somewhat less than under the previous conditions, but that the modulus of compression, while somewhat less at the lower densities, is decidedly greater at the higher, showing that the departures of formula (74) from (25), which it replaces, have qualitatively the character shown to be needed. Of the energy-totals,  $\Phi_h$  is necessarily the same as before, while  $\Phi$  and E are respectively 1.2 per cent and 14.1 per cent less than their former values, so that relatively more of the primitive energy is transformed by impact and lost by radiation. This is obviously due to the greater mass of the nucleus, at a given radius, and the correspondingly larger velocity of impact in this as compared with the former case.

TABLE 9.

2	P	10—12 p	10-12 H	<u>5e</u> J
0.00	9.65	2.80	7.39	16,610
.05	9.64	2.79	7.36	16,540
.10	9.58	2.75	7.25	16,360
.15	9.50	2.68	7.08	16,050
.20	9.38	2.59	6.85	15,630
.25	9.22	2.48	6.56	15,090
.30	9.03	2.35	6.22	14,430
.35	8.81	2.20	5.83	13,670
.40	8.55	2.03	5.44	12,810
.45	8.26	1.85	4.94	11,850
.50	7.93	1.66	4.45	10,800
.55	7.57	1.46	3.95	9,680
.60	7.17	1.27	3.45	8,500
.65	6.74	1.07	2.95	7,260
.70	6.27	.88	2.47	5,990
.75	5.77	.69	2.01	4,720
.80	5.24	.52	1.58	3,460
.85	4.67	.36	1.19	2,260
.90	4.07	.22	.86	1,190
.95	3.43	.10	.57	<b>'36</b> 0
1.00	2.76	.00	.34	0

Table 9, based on the formula  $\rho = \rho_0(1 - \frac{\epsilon}{2}x^2)$ , gives the values at various depths of the density, of the pressure and bulk-modulus in millions of atmospheres, and the thermal measure for  $\sigma = 0.2$  of the specific compressional energy.

To estimate the modifications in the thermal process due simply to the change in the formula for density, it will be well to repeat the former alternative hypotheses regarding the specific heat.

If  $\sigma$ ,  $\lambda$  are constant, the primitive temperature-curve by (78) is

$$\theta = \theta_0 \left( 1 - x^2 \right)^2 \left( 1 - \frac{1}{5} x^2 \right) \div \left( 1 - \frac{5}{7} x^2 \right) \qquad \theta_0 = \frac{e_0}{\sigma J} \tag{82}$$

which is tabulated in column 5 of table 9, while equation (55) reduces to

$$\frac{1}{x^2} \frac{d}{dx} \left( x^2 \frac{dy}{dx} \right) + \mu \left( 1 - cx^2 \right) y = 0 \tag{83}$$

giving for the fundamental functions

$$y = \sum_{i=0}^{i=\infty} (-1)^i a_i x^{2i}$$
 (84)

where the coefficients  $a_i$  are determined successively from

$$a_0 = 1$$
  $a_1 = \frac{\mu}{6}$   $a_i = \frac{\mu}{2i(2i+1)}(a_{i-1} + ca_{i-2})$   $i = 2 \dots \infty$  (85)

with the values of  $\mu$  which make y vanish at x=1. The complete computation to sufficient accuracy to determine the details of the conduction is again hardly practicable, but the first two fundamental functions with their parameters  $\mu$ ,  $\tau$ , and coefficients A determined from (56) are:

$$y_{1} = 1 - 2.04360 \ x^{2} + 1.69080 \ x^{4} - .91977 \ x^{8} + .36231 \ x^{8} - .11362 \ x^{10} + .02927 \ x^{12} - .00645 \ x^{14} + .00123 \ x^{16} - .00021 \ x^{18} + .00003 \ x^{20} - . . . .$$

$$\mu_{1} = 12.2616 \qquad A_{1} = 1.089 \ \theta_{0} \qquad \tau_{1} = 400 \text{ billion years}$$

$$y_{2} = 1 - 8.59393 \ x^{2} + 23.99826 \ x^{4} - 36.99908 \ x^{6} + 38.77346 \ x^{8} - 30.56380 \ x^{10} + 19.25673 \ x^{12} - 10.08879 \ x^{14} + 4.52008 \ x^{16} - 1.76799 \ x^{18} + .61344 \ x^{20} - .19120 \ x^{22} + .05409 \ x^{24} - .01400 \ x^{26} + .00334 \ x^{26} - .00074 \ x^{20} + .00015 \ x^{22} - .00003 \ x^{34} + . . . .$$

$$\mu_{2} = 51.5636 \qquad A_{2} = -.0705 \ \theta_{0} \qquad \tau_{2} = 96 \text{ billion years}$$

These are given in table 10, columns 2 and 3, together with the residuals from the primitive curve due to components higher than the first and second respectively in columns 4 and 5, the tabulation in all cases using as unit the primitive central temperature  $\theta_0$ , which for  $\sigma=0.2$  is about 16,600°. The last column of that table gives the initial rate of change of temperature, computed from

$$\frac{\partial \theta}{\partial t} = \frac{\theta_0 \lambda}{\sigma \rho_0 r_1^2} \left\{ -\frac{312}{35} + \frac{1268}{49} x^2 - \frac{132}{5} x^4 + 12 x^6 - \frac{100}{49} x^4 \right\} \div \left\{ 1 - \frac{5}{7} x^2 \right\}^2 \tag{87}$$

which follows from (52) and (82), the tabulation using, however, as unit of measure the value of  $\frac{\theta_0 \lambda}{\sigma \rho_0 r_1}$ , equivalent to a change of about  $3\frac{1}{2}$ ° in a billion years.

TABLE 10.

x	<b>y</b> 1	3/2	F (z)	$F_1(x)$	$F_{\mathbf{i}}(x)$	80 86
0.00	1.0000	1.0000	1.0000	-0.0890	-0.0185	— 8.91
.05	.9949	.9787	.9963	<b>—</b> .0871	<b>— .0181</b>	<b>— 8.90</b>
.10	.9797	.9164	.9852	0817	<b>— .0171</b>	<b>— 8.85</b>
.15	.9549	.8184	.9668	<b>—</b> .0731	0154	<b>— 8.76</b>
.20	.9209	.6924	.9411	<b>— .0618</b>	<b>— .0130</b>	8.64
.25	.8787	.5482	.9085	<b>—</b> .0484	0098	<b> 8.48</b>
.30	.8291	.3963	.8691	<b>— .0338</b>	<b>0059</b>	8.29
.35	.7734	.2473	.8232	0190	0016	8.05
.40	.7128	.1103	.7712	0050	+ .0028	<b>— 7.77</b>
.45	.6484	0074	.7134	+ .0072	→ .0067	<b>— 7.45</b>
.50	.5817	1009	.6505	+ .0170	+ .0099	<b>— 7.06</b>
.55	.5138	1679	.5830	+ .0234	+ .0116	6.62
.60	.4460	<b>— .2083</b>	.5117	+ .0260	+ .0113	6.08
.65	.3792	2243	.4373	+ .0243	+ .0085	- 5.45
.70	.3144	2194	.3609	+ .0185	+ .0030	4.66
.75	.2525	1981	.2840	+ .0091	0049	- 3.64
.80	.1938	1653	.2082	0029	0145	- 2.27
.85	.1392	1255	.1361	0154	0242	- 0.26
.90	.0886	0827	.0718	0246	0304	+ 3.00
.95	.0422	0401	.0219	0240	0268	+ 9.01
1.00	.0000	0000	.0000	.0000	.0000	+22.40

In table 10, based on the hypothesis  $\sigma = \sigma_0$ ,  $\lambda = \lambda_0$ ,  $\rho = \rho_0 (1 - \frac{5}{7} x^2)$ , the functions  $y_1$ ,  $y_2$  are the first two fundamental functions; F(x) gives the primitive temperature-curve,  $F_1(x) = F(x) - A_1 y_1$ ,  $F_2(x) = F_1(x) - A_2 y_2$ ; in each the temperatures and coefficients A are expressed in terms of the unit  $\theta = 16,600^{\circ}$ . The last column gives the initial rate of the change of temperature in terms of a unit corresponding to a change of  $3\frac{1}{2}$  in a billion years; the entries in this column must be multiplied by  $\frac{\theta_0 \lambda}{\sigma \rho_0 r_1^2}$  to be reduced to absolute units.

Comparison of this table with table 5 shows that the change in distribution of the density makes no striking change in the thermal process. The second component has a larger coefficient, and the residuals left by the first two components are somewhat smaller. But these residuals have in general the same trend, and together with the values of  $\frac{\partial \theta}{\partial t}$  indicate the same initial partition of the mass into inner and outer regions of falling and rising temperature, respectively. The outer zone is, however, shallower than under the former case, extending at the start to a depth of not quite 600 miles. The increase in the tabulated values of the initial rate  $\frac{\partial \theta}{\partial t}$  and of the gradient of the first component for points near the surface, together with the coefficient  $A_2$ , is offset by the decreased value of  $\theta_0$ , in terms of which the entries are expressed, so that the maximum temperature-gradient at the surface occurring when the zone of rising temperature disappears, would be

probably about as before. The time-scale of the phenomena can be considered practically the same as before, especially in view of the uncertainty as to the appropriate values of the thermal constants.

Under the other supposition, that  $\lambda$  and  $\sigma\rho$  are constant, the fundamental functions are again defined by (67), while the primitive temperature is

$$\theta = \theta_0 (1 - x^2)^2 (1 - \frac{1}{5} x^2) \tag{88}$$

where now

$$\theta_0 = \frac{e_0}{\sigma_1 J} \cdot \frac{\rho_0}{\rho_1} \tag{89}$$

or about 58,000°. The coefficients of the series are given by

$$A_n = 2 (-1)^{n-1} \left\{ -\frac{32}{5n^2\pi^2} + \frac{1008}{n^6\pi^6} \right\}$$
 (90)

the first few of which are:

$$A_1 = 0.80006$$
  $A_2 = 0.29146$   $A_4 = 0.08054$   $A_6 = 0.03598$   $A_5 = -0.14122$   $A_5 = -0.05174$   $A_7 = -0.02645$ 

the alternation in sign and steady decline in numerical value continuing throughout.

The time-interval T, during which the first component declines by 1 per cent, is the same as with the former density formula, or about  $1\frac{1}{2}$  billion years, with the thermal constants assumed. The effect of the conduction in modifying the distribution of temperature is indicated in table 11, for epochs differing by five such intervals. To the order of accuracy for this table the numbers of components of sensible influence range from about 100 for the earliest epoch to 4 for the latest given.

TABLE 11.

				IABUM I	••			
z	<b>0</b> (0)	● (5T)	# (10T)	0 (15T)	● (20T)	● (25 T)	# (80T)	# (85 T)
0.00	1.0000	0.9349	0.8741	0.8174	0.7646	0.7156	0.6703	0.6285
.05	.9945	.9298	.8693	.8129	.7604	.7118	.6668	.6252
.10	.9782	.9145	.8550	.7996	.7481	.7003	.6562	.6155
.15	.9512	.8893	.8315	.7777	.7278	.6815	.6388	.5994
.20	.9142	.8547	.7993	.7477	.6999	.6558	.6151	.5776
.25	.8679	.8115	.7590	.7103	.6653	.6238	.5856	.5504
.30	.8132	.7604	.7115	.6663	.6246	.5862	.5509	.5184
.35	.7512	.7026	.6578	.6166	.5787	.5439	.5119	.4825
.40	.6830	.6393	.5992	.5624	.5287	.4979	.4696	.4435
.45	.6102	.5718	.5368	.5050	.4760	.4494	.4249	.4022
.50	.5344	.5018	.4723	.4456	.4215	.3993	.3787	.3595
.55	.4571	.4306	.4070	.3858	.3666	.3488	.3321	.3164
.60	.3801	.3601	.3426	.3270	.3126	.2990	.2860	.2735
.65	.3053	.2919	.2807	.2705	.2607	.2509	.2412	.2316
.70	.2346	.2281	.2228	.2175	.2117	.2053	.1985	.1914
.75	.1698	.1702	.1704	.1691	.1664	.1627	.1582	.1533
.80	.1130	.1198	.1242	.1258	.1253	.1234	.1207	.1174
.85	.0659	.0781	.0848	.0876	.0883	.0877	.0862	.0841
.90	.0303	.0453	.0516	.0545	.0555	.0554	.0547	.0535
.95	.0078	.0201	.0239	.0255	.0262	.0263	.0260	.0255
1.00	0	0	0	0	0	0	0	0

Here the zone of rising temperature extends at first to a depth of a little over 1,000 miles, and the chief features of its history may be thus summarized:

TABLE 12.

æ	Depth in miles.	Epoch of maximum temperature.	Initial temperature.	Total rise.
0.75	1,000	8.3 T	9,870°	40°
.80	800	16.3 T	6,570°	7 <b>4</b> 0°
.85	600	20.1 T	3,830°	1,300°
.90	400	22.2 T	1,760°	1,470°
.95	200	23.5 T	450°	1,080°

The rising temperatures finally cease at epoch about 24 T, with the attainment of a maximum surface gradient of 1° in about 220 meters.

To complete the sketch of the modified theory, in a way parallel to that of Part I, there might be traced an analogous history of the nucleus during the period of accretion, supposing the compressibility of the substance to correspond to equation (76). But in contrast with (25) it must be noticed that this could not be done by treating (74) as the general expression for the density at every epoch. For by (76) the modulus of compression has the form  $H = h\rho + h'\rho^2 \tag{91}$ 

and if this is to be definite and characteristic of the substance, not dependent on the dimensions of the mass into which it may be gathered, the coefficients h, h' must be numbers depending only on the units of measure used, which on account of the manner of their dependence on  $\rho_0$  and c can be so only if the latter also are particular numbers in the same sense, not arbitrary parameters depending on the size of the body. The general expression for the density would have to be sought by integration of equation (6) with the condition (91), which would yield a family of curves corresponding to the nucleus at various stages, but of which only the final one has the simple parabolic form defined by (74). The general integral would contain two constants, but one may be considered eliminated either to make the density finite at the center or by the condition that  $\frac{d\rho}{dr}$  vanish at the center. For this particular law of compressibility the general integral does not appear to be known in form sufficiently simple to make the computation practicable.

This suggests that in connection with the planetesimal hypothesis it would be convenient to have a series of examples of curve-families, each of which could be considered to represent the distribution of density at the various stages of aggregation of a substance with a certain definite law of compressibility—equations simple enough to allow the detailed computations, but so varied as to admit of choice in adapting to other accepted data. As a help towards the discovery of such it may be asked what general condition a family of density-curves must satisfy in order that a definite compressibility may be deduced.

This condition means that if the curves be supposed given in the form

$$\rho = f(r, a) \tag{92}$$

where a is the parameter of integration, whose value corresponds, for instance, to the total radius or the central density, then the modulus H deduced therefrom must be a function of  $\rho$  only, independent of a. Equations (3), (4), (5), (15) show this to be equivalent to the condition that

 $\frac{m}{r^2 \frac{d\rho}{dr}}$  shall be a function of  $\rho$  only, or in terms of the functional determinant

$$\begin{vmatrix} \frac{\partial}{\partial r} \left( \frac{m}{r^2 \frac{\partial \rho}{\partial r}} \right) & , & \frac{\partial \rho}{\partial r} \\ \frac{\partial}{\partial a} \left( \frac{m}{r^2 \frac{\partial \rho}{\partial r}} \right) & , & \frac{\partial \rho}{\partial a} \end{vmatrix} = 0$$
 (93)

in which is put, as before

$$m = 4\pi \int_{A}^{r} \rho r^2 dr$$

By differentiation and elimination of m this fundamental condition can be reduced to a partial differential equation for  $\rho$ , in rather cumbersome form. Trial shows that (74) is not a solution for any manner of dependence of  $\rho_0$  and c on a; but (25) is a solution, if  $\rho_0$  be a function of a, and q a numerical constant.

Another special solution of (93) in simple form is found to be

$$\rho = a^5 \left( 1 + \frac{1}{3} a^4 \mu^2 r^2 \right)^{-\frac{5}{2}} \qquad \mu = \text{const.}$$
 (94)

for which

$$m = \frac{4}{3} \pi r^3 a^5 \left( 1 + \frac{1}{3} a^4 \mu^2 r^2 \right)^{-\frac{8}{2}}$$
 (95)

so that for various values of a it would give the density curves for masses of different dimensions, if the substance were to satisfy the condition

$$\frac{dp}{d\rho} = h\rho^{\frac{1}{5}} \qquad h = \frac{4\pi k}{5\mu^2} \tag{96}$$

With such a substance the compressibility at various densities would be such that not only would there be a definite limit to the dimensions which the mass could attain, but this would be reached with a finite mass, and beyond that point any further addition of strata at the surface would result in an actual decrease in size, as appears from the following analysis.

If  $\rho_m$ ,  $\rho_1$ ,  $r_1$  be the mean and surface densities and total radius at any chosen epoch, and  $a_1$  the corresponding value of a, then

$$\rho_{\mathbf{m}} = a_1^{\ 6} \left( 1 + c \right)^{-\frac{3}{2}} \tag{97}$$

$$\rho_1 = a_1^{5} (1+c)^{-\frac{5}{2}} \tag{98}$$

where

$$c = \frac{1}{3} a_1^4 \mu^2 r_1^2$$

whence

$$\frac{\rho_{\rm m}}{\rho_{\rm i}} = 1 + c \tag{99}$$

Then since the surface density is not to change, the total radius  $r_1$  and the parameter a at any epoch are related by

$$\rho_1 = a^5 \left\{ 1 + cA^2 R \right\}^{-\frac{5}{2}} \tag{100}$$

which, combined with (98), gives

$$RcA^{2}-(1+c)A+1=0$$
 (101)

a quadratic equation for A, in which are put

$$A = \left(\frac{a}{a_1}\right)^2 \qquad R = \left(\frac{r_1'}{r_1}\right)^2$$

The condition for reality of the roots shows that the maximum possible radius is

$$r_1' = \frac{r_1}{2} \cdot \frac{1+c}{\sqrt{c}}$$
 (102)

as may be deduced also from the transformed equation

$$R = \frac{(1+c)A - 1}{A^2} \tag{103}$$

From which it is seen that R as a function of A has a maximum value  $R = \frac{(1+c)^2}{4c}$  at  $A = \frac{2}{(1+c)}$ . As A increases indefinitely from its smallest admissible value, which is  $\frac{1}{1+c}$ , the mass also increases from zero without limit, but the total radius increases to the maximum value indicated and then decreases toward zero. For any assigned radius less than the maximum there would thus be two possible distributions of density, giving masses less than and greater than the critical mass, and with mean densities less and greater than double the surface density respectively.

If, however, the constants  $a_1$ , c be determined by (97), (98), from the values of  $\rho_m$ ,  $\rho_1$  heretofore assumed for the earth, the computation according to (94) shows that for some distance downward from the surface the density would increase more slowly than with either of the formulæ used before, but then rise more rapidly and at the center reach a value of 15 to 16. In view of the probable corrections mentioned above as needed to change the Laplacian formula into one agreeing better with the data available, it appears that in comparison with (25) the formula (94) is much less satisfactory, as an approximation to the general distribution of density

within the earth. It is here dwelt on briefly for the sake of the comparison it affords with still another now to be considered, which also belongs to the class for which

 $\frac{dp}{da} = h\rho^{n} \tag{104}$ 

of which (20) and (96) are examples.

It was shown in Part I that, with the particular law of compressibility there postulated, the progressive condensation under the increasing load of the material gathered at the surface would be accompanied by a deformation of the elements of the mass whose final amount is indicated by the distortion-factor tabulated. Attention was called to the consequent uncertainty introduced into the determination of the work of compression if it be supposed that the substance offers appreciable resistance, either elastic or viscous, to shearing stresses, so that the working pressure is not purely hydrostatic. It is conceivable, however, that this deformation might be widely different in character and amount under another acceptable pressure-density law, so that the acceptance of the special formulas (20) and (25) would lead to no just estimate of the essential obscurity in the theory from this source.

As a guide to conjecture on this point it will be of interest to determine whether there could be a law of compressibility assumed of such nature that the condensation of the mass would lead to no such deformation, but rather that the compression would be at all points purely cubical.

If x be an auxiliary variable, determining the location of a given particle at some chosen epoch, for instance as before the ratio of the ultimate distance from the center to the total radius, then the distance r from the center at any epoch may be considered as a function of a and x:

$$r = \psi(a, x) \tag{105}$$

Let x', x'' be the values of x corresponding to two chosen particles; then the mass of the spherical shell whose bounding surfaces pass through those particles will be

$$m(x', x'') = 4\pi \int_{x'}^{x''} \rho r^2 \frac{\partial r}{\partial x} dx$$
 (106)

As the condensation progresses the spherical surfaces will shrink, but the mass between them must remain constant. This means that the integral (106) must be independent of a, whatever the values of x', x''; this gives the condition

$$\frac{\partial r}{\partial x} \left\{ r^2 \left( \frac{\partial \rho}{\partial a} + \frac{\partial \rho}{\partial r} \frac{\partial r}{\partial a} \right) + 2\rho r \frac{\partial r}{\partial a} \right\} + \rho r^2 \frac{\partial^2 r}{\partial a \partial x} = 0$$

which reduces to

$$r\left\{\frac{\partial\rho}{\partial a} + \frac{\partial(\rho P)}{\partial r}\right\} + 2\rho P = 0 \tag{107}$$

in which is put

$$P(a,r) = \frac{\partial r}{\partial a} \tag{108}$$

obtained from (105) by differentiation and elimination of x, which is admissible, since r is a monotonic function of x.

Moreover, the variations in horizontal and vertical dimensions of a given element of the mass are proportional to the variations of r and of  $\frac{\partial r}{\partial x}$  respectively as functions of a. The condition of no distortion demands therefore that  $\frac{1}{r} \frac{\partial r}{\partial x}$  shall be independent of a, which gives

$$\frac{1}{r}\frac{\partial P}{\partial r} - \frac{P}{r^2} = 0 \tag{109}$$

so that P may be written in the form

$$P = -rQ(a) \tag{110}$$

showing that, to satisfy the conditions named, a differential accretion at any epoch must depress each particle an amount proportional to its distance from the center, but so that the factor of proportionality depends in an indetermined way on the momentary total dimensions of the body.

The last equation reduces (107) to

$$r\frac{\partial\rho}{\partial r} - \frac{1}{Q}\frac{\partial\rho}{\partial a} + 3\rho = 0 \tag{111}$$

of which the general solution is

$$\rho = \frac{1}{r^3} \varphi'(\zeta) \tag{112}$$

where

$$\zeta = \log r + \int Q \, da \tag{113}$$

The mass within the radius r is then

$$m = 4\pi \,\varphi(\zeta) \tag{114}$$

provided that in the function  $\varphi$ , whose derivative is the arbitrary function  $\varphi'$  in (112), the additive constant be chosen suitably, which the finiteness of the mass would show to be possible.

It remains to impose the condition that the substance have a definite compressibility. Equations (112) and (114) yield

$$\frac{1}{\rho}\frac{dp}{d\rho} = -4\pi k \frac{r^2 \varphi}{\varphi'' - 3\varphi'} \tag{115}$$

and this must be a function of  $\rho$  only. This is equivalent to the condition that if  $\phi = \frac{\varphi'' - 3\varphi'}{\varphi}$ 

then  $r^{-2}\theta$  and  $r^{-3}\varphi'$  must be dependent functions of r,  $\zeta$ ; or in terms of the functional determinant

functional determinant  $\frac{1}{r^3} \begin{vmatrix} 20 & 0' \\ 3\varphi' & \varphi'' \end{vmatrix} = 0$ 

This could be obtained from the general equation (93) by substitution of (112) and change of variables from r, a to r,  $\zeta$ . It shows that, with C an arbitrary constant, the relation must have the form

$$\Phi^3 = C^3 \varphi'^2$$

giving for determination of the function  $\varphi$ 

$$\varphi'' - 3\varphi' = C\varphi\varphi'^{\frac{3}{2}} \tag{116}$$

on account of which (115) gives for the equation characteristic of the substance

$$\frac{dp}{d\rho} = h\rho^{\frac{1}{2}} \qquad h = -\frac{4\pi k}{C} \tag{117}$$

so that C must be negative. This is, then, the condition which it is necessary that the substance satisfy in order that the condensation under increasing mass may not be accompanied by distortion of the mass-elements.

Conversely, if the substance satisfy this condition, the compression will take place without deformation. For, with the substitution of (117), equation (6) takes the form

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \mu^2 R^2 = 0 \qquad \mu^2 = \frac{4\pi k}{3h} \qquad R^3 = \rho$$
 (118)

The solution which is finite at the center has the form

$$R = R_0 \mathcal{Q}(u) \qquad \qquad R_0^3 = \rho_0 \qquad \qquad u = R_0 \mu r \tag{119}$$

where Q is a definite function, which for sufficiently small values of u can be expanded as a power series with numerical coefficients of alternate signs

$$Q(u) = 1 - B_1 u^2 + B_2 u^4 - \dots$$

If the radius of convergence be too limited, the function may be considered as determined for any value of u by analytic continuation, since equation (118) has no singularities to prevent. The density is then

$$\rho = \rho_0 \omega(u) \qquad \qquad \omega(u) = [\Omega(u)]^3 \qquad (120)$$

so that  $\omega$  also is expansible for small values of u as an alternating series with numerical coefficients

$$\omega(u) = 1 - b_1 u^2 + b_2 u^4 - \dots$$

Then

$$m = 4\pi \rho_0 \int_0^u r^2 \omega (u) \frac{dr}{du} du$$

whence

$$m = \frac{4\pi}{\mu^3} \; \theta(u) \tag{121}$$

where  $\theta$  is the definite function

$$\theta(u) = \int_{0}^{u} u^{2}\omega(u)du \tag{122}$$

or as power-series

whence

$$\theta(u) = \frac{1}{3} u^3 - \frac{1}{5} b_1 u^5 + \frac{1}{7} b_2 u^7 - \dots$$

Since  $\mu$  is in effect a physical constant of the material, equation (121) shows that any particular value of u will determine a spherical surface, of varying radius according to the varying value of  $\rho_0$ , but always passing through the same material particles, so as to inclose the mass determined by that equation. If, then, u, v be two values of u corresponding to two definite particles,  $\alpha'$ ,  $\beta'$  and  $\alpha''$ ,  $\beta''$ , their distances from the center at two stages of the compression when the central densities are  $\rho_0'$ ,  $\rho_0''$  respectively, then the definition of u gives

$$u = \rho_0^{\prime \dagger} \mu \alpha^{\prime} = \rho_0^{\prime \prime \dagger} \mu \alpha^{\prime \prime} \qquad v = \rho_0^{\prime \prime \dagger} \mu \beta^{\prime} = \rho_0^{\prime \prime \dagger} \mu \beta^{\prime \prime}$$

$$\frac{\alpha^{\prime}}{\beta^{\prime}} = \frac{\alpha^{\prime \prime}}{\beta^{\prime \prime}} \qquad (123)$$

showing that the distances of two particles from the center remain in the same ratio as the condensation progresses. This is precisely the kind of contraction by which distortion of elements is avoided.

The constant  $\mu$  would be determined by the mean and surface densities at a given epoch from the equations

$$\rho_{1} = \rho_{0}\omega(u_{1}) \qquad \rho_{m} = 3\rho_{0}\frac{\theta(u_{1})}{u_{1}^{2}} \qquad u_{1} = \rho_{0}^{2}\mu\sigma_{1} \qquad (124)$$

which would yield also the central density  $\rho_0$  at that epoch; then for any epoch the first of these would determine the central density for any assigned total radius.

The determination of the exact distribution of density under these conditions would rest on the computation of the coefficients so that R satisfies the differential equation (118); but a sufficient idea of the curve may be gathered simply by comparison of formula (117) with (96) and (20). All of these belong to the class (104), with exponents  $\frac{1}{3}$ ,  $\frac{1}{5}$ , and 1 respectively, so that the first is a sort of average of the other two. With the same assigned mean and surface densities, it may be inferred that the hypothesis now considered would result in densities less in the outer strata and greater in the central portion than those given by the Laplacian formula (25), but deviating in that way to a less extent than those computed from (94). Such departures are opposite to the corrections which the Laplacian law seems to require, though the data from observation are but meager; so that (117) must probably be rejected, as not giving a satisfactory approximation to the actual distribution of density within the earth. The only satisfactory curves of class (104) would seem to be those with exponents somewhat larger than unity.

The intermediate character of (117) as compared with (20) and (96) appears also in the phenomena which would attend unlimited accretion.

Equations (117) and following, combined with the hydrostatic equation (3), give

$$\frac{dQ}{du} = -\frac{\theta}{u^2}$$

and (122) gives

$$\frac{d\theta}{du} = u^2 Q^2$$

from combination of which comes

$$\frac{dz}{dy} = \frac{z - y}{z^2} \qquad y = \theta \qquad z = uQ \tag{125}$$

This equation determines a family of curves in the y-z plane, of which the one required for the present purpose passes through the origin, at which the z-axis is an inflectional tangent. In the neighborhood of the origin this curve is given by the expansion

$$y = \frac{1}{3}z^{5} + \frac{1}{15}z^{5} + \frac{8}{315}z^{7} + \dots$$
 (126)

with coefficients all positive. The arc required is that lying in the quadrant where y and z are positive.

In the half-quadrant where y>z, the inequality  $\frac{dy}{dz}>z^2$  gives  $y>\frac{z^3}{3}$ , which shows that the curve reaches the line y=z at some point (a,a)such that  $0 < a < \sqrt{3}$ . Crossing this line, with tangent parallel to the yaxis, the curve passes into the half-quadrant where y>z, where the inequality  $\frac{dz}{dy} < \frac{a-y}{z^3}$  gives  $z^4 < a^4 - 2(y-a)^4$ , which shows that the curve must cross the y-axis, with tangent parallel to the z-axis, at a point  $(z=0, y-\beta)$ such that  $\beta < \alpha + \frac{\alpha^2}{\sqrt{2}}$  or  $\beta < \alpha(1 + \frac{1}{2}\sqrt{6})$ . The curvature does not change

sign in this quadrant, since the differential equation gives

$$\frac{d^2z}{dy^2} = -[3(z-y)^2 - z(z-y) + z^4] + z^7$$

which is constantly negative where y and z are positive. This part of the curve is therefore a simple arch concave to the y-axis and crossing perpendicularly at y=0 and at  $y=\beta$ .

This means that there is a finite critical mass which is reached only when the function  $\omega(u)$  becomes zero and consequently the density at the center infinite. The corresponding value of u is then infinite, but the radius is finite, since the density must be everywhere greater than  $\rho_1$ . This result may be compared on the one hand with the case  $n = \frac{1}{5}$ , where the limiting radius is reached while the mass and central density are both finite; on the other hand with the case n=1, where the limiting radius is approached only asymptotically as the mass increases indefinitely.

From the rejection of the hypothesis last developed it appears, therefore, that under the law of compressibility which would result from any acceptable density-formula the compression in the interior as the mass increased would inevitably be accompanied by local deformations, resulting from the inequality of vertical and horizontal compression, and probably in character and magnitude similar to those described in Part I. Thus the theory developed from the hydrostatic equations remains subject to the uncertainty from this source in the computation of the compressional energy, to an extent not easy to estimate.

The thermal process has thus far been outlined on two alternative suppositions regarding the variation of  $\rho$ , and two regarding  $\sigma$ , but in all cases the conductivity was treated as constant. This condition might be replaced by the supposition often made that it increases from the surface toward the center on account of the increasing condensation of the material. Such a variation would have the effect of facilitating the transfer of heat from the interior to the superficial strata, probably raising the maximum gradient of temperature attained near the surface and perhaps shortening the time during which the temperature has anywhere an upward trend. The effect on the depth of the region where  $\frac{\partial \theta}{\partial t}$  is at first positive is seen by inspection of equation (52), which can be written

$$\frac{\partial \theta}{\partial t} = \frac{\lambda}{\sigma \rho} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \theta}{\partial r} \right) + \frac{1}{\lambda} \frac{\partial \theta}{\partial r} \frac{\partial \lambda}{\partial r} \right\}$$

In the second member, the first term, which alone has occurred hitherto, is positive in the outer region and negative in the interior;  $\frac{\partial \theta}{\partial r}$  is every-

where negative, while if  $\lambda$  increases toward the interior  $\frac{\partial \lambda}{\partial r}$  is negative, making the second term positive. This shows that the zone of rising temperature would be deeper than with constant  $\lambda$ , with the same original temperature curve. The more improbable supposition that  $\lambda$  decreases toward the interior would have the contrary effect, but, as will be seen presently, could by no means eliminate the outer zone entirely.

The fact that under a variety of suppositions regarding the thermal coefficients  $\rho$ ,  $\sigma$ ,  $\lambda$  there occurs a thermal process marked by the same general features, even with no radical differences in order of magnitude in the numerical data, suggests that those features are not dependent on such special hypotheses, but due to the general properties of the original distribution of temperature and characteristic of its mode of origin. The following general considerations show why they may be expected to persist under any hypotheses on  $\rho$ ,  $\sigma$ ,  $\lambda$ , not differing too radically from those developed above.

Whatever may be the actual variations of  $\rho$ , g,  $\sigma$ ,  $\lambda$ , any equations assuming to represent them as functions of r only can hardly be treated as more than interpolation-formulas, representing the gross features of the concrete situation in the sense of averages, and disregarding the relatively trivial local variations on account of which it is only to a certain degree of accuracy that there can be said to be, for instance, a definite law of density at all. It seems, therefore, practically general to assume in the neighborhood of the

surface a representation in series ascending powers of  $s=r_1-r_2$ , in the form

$$\rho = \rho_1 + a_1 s + a_2 s^2 + \dots$$

$$\sigma = \sigma_1 + c_1 s + c_2 s^2 + \dots$$

$$g = g_1 + b_1 s + b_2 s^2 + \dots$$

$$\lambda = \lambda_1 + d_1 s + d_2 s^2 + \dots$$

such that a few terms suffice to give all the precision which has useful meaning under the circumstances. From these come

$$\frac{dp}{ds} = g\rho = g_1\rho_1 + (g_1a_1 + \rho_1b_1)s + \dots$$

$$p = g_1\rho_1s + \frac{1}{2}(g_1a_1 + \rho_1b_1)s^2 + \dots$$

$$\frac{p}{\rho^2} = \frac{g_1}{\rho_1}s + \frac{\rho_1b_1 - 3g_1a_1}{2\rho_1^2}s^2 + \dots$$

$$e = \int_{a}^{b} \frac{p}{\rho^2} \frac{d\rho}{ds} ds = \frac{g_1a_1}{2\rho_1}s^2 + \dots$$

so that the temperature-curve in the neighborhood of the surface has the form

$$\theta = Cs^2 + \dots \qquad C = \frac{g_1a_1}{2\rho_1\sigma_1J}$$

and is consequently tangent to the x-axis at the surface-point x=1. The tangency is of ordinary parabolic type, since the vanishing of  $a_1$  would mean that the surface material was incompressible. The temperature at first changes at rate

$$\frac{\partial \theta}{\partial t} = \frac{1}{\sigma \rho} \cdot \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left( \lambda r^2 \frac{\partial \theta}{\partial r} \right) = \frac{2C\lambda_1}{\sigma_1 \rho_1} + \text{terms with factor } (r - r_1)$$

Since the first term here is essentially positive, there is necessarily a region just below the surface where the temperature rises.

On the other hand, at the center there occur maxima of the curves for p,  $\rho$ , and consequently for e. This would most probably happen also for  $\theta$ , so that the appropriate expansion would be of the form

$$\theta = \theta_{\bullet} - Cr^2 \dots$$

with which the initial rate of change is

$$\frac{\partial \theta}{\partial t} = -\frac{6C\lambda_0}{\sigma_0\rho_0} + \text{terms with factor } r^2$$

the first term of which is essentially negative, so that the temperature falls in the neighborhood of the center. The only case in which this would not happen would be when  $\sigma$  would have a maximum at the center, strong enough to throw the maximum of temperature to a point further out, which is highly improbable, a necessary condition for this being that with expansions of the type

$$\rho = \rho_0 (1 - b_1 r^2 \dots)$$
  $\sigma = \sigma_0 (1 - c_1 r^2 \dots)$ 

the coefficients satisfy the inequality  $\frac{c_1}{b_1} \ge \frac{p_0}{\rho_0 c_1}$ 

These results do not exclude the occurrence of more than two sones, alternating with fall and rise of temperature, but inspection of the analogous expansions for intermediate points seems to indicate that this would demand variations of  $\rho$ ,  $\sigma$ ,  $\lambda$  which differ widely in character from those thus far postulated, and which are perhaps improbable, but whose probability it is difficult to estimate with the meager data at hand.

Comparison of the various cases carried out in the computations gives a fairly definite idea of a thermal process which, from the general point of view hitherto adopted, can be considered characteristic of the planetesimal hypothesis so far as concerns independence of particular hypotheses respecting the density, conductivity, and specific heat. Under the basic assumptions made, the balance of evidence seems to favor its substantial correctness in qualitative features, and even in general order of numerical magnitudes, since the chief allowances to be made in the latter can be estimated with confidence from the theory itself. For example, the lengths of time involved may be overrated, about in the ratio that the true conductivity in the interior surpasses, as it probably does, the value used, which is that obtained by observations on the rather loosely aggregated material accessible at the surface.

There seems to be sufficient reason for supposing the energy of impact to have little influence in determining the primitive temperature, especially if the impinging particles be retarded seriously by an atmosphere. But aside from this there have been made certain general assumptions, which, though fundamental in the foregoing theory, seem to be arbitrary rather than essential to the general hypothesis, and thus to demand critical examination. This will be attempted in Part III, in connection with the development of an alternative theory intended to aid in estimating the allowance which should be made for possible modifications of some of these.

## PART III.—THERMODYNAMIC THEORY.

As a strict theory, the foregoing deductions imply a sort of ideal earth-substance, with respect to which certain assumptions are made, in a form convenient for the purpose in hand, but not sufficient to define completely its thermodynamic properties. How closely they represent the actual behavior of the substances composing the earth's interior is largely conjecture, in view of the meagerness and limited range of direct experimental information; but they may be examined as to their consistency with accepted thermodynamic laws regarding the interplay of thermal and mechanical processes.

It has been supposed that a general idea of the thermal process, after the earth was completely formed, could be obtained by treating it as a matter of pure conduction and accompanying radiation at the surface. But the significance for geological theory of the redistribution of heat lies largely in the resulting expansions or contractions in different portions of the mass, and these geometric changes would in general involve the passage of energy between the mechanical and the thermal form, in amount perhaps by no means negligible in comparison with the heat conducted. In particular, if the temperature should on the average fall, the energy thus lost would be partly compensated by that developed out of gravitational work during the contraction.

As to the possible relative magnitude of these, as it were, opposing movements of energy, a summary estimate may be gathered from the case of a homogeneous sphere at uniform temperature, contracting so as to remain such, and supposed to have specific heat and coefficient of expansion constant throughout. In this case the energy developed by ingathering from infinite dispersion is

$$\theta = \frac{3}{5} k \frac{m^2}{r}$$

while the thermal content is

$$Q = m\sigma\theta J$$

from which come

$$-\frac{d\theta}{dr} = \frac{3}{5} k \frac{m^2}{r^2} \qquad \frac{dQ}{d\theta} = m\sigma J$$

while

$$\frac{dr}{d\theta} = \frac{a}{3}r \qquad \frac{dQ}{dr} = \frac{3moJ}{a}$$

where a is the volume coefficient of expansion, or three times the linear coefficient; so that

$$-\frac{d\theta}{dQ} = \frac{kma}{5roJ} \tag{127}$$

which is the ratio of the gain of energy from the gravitational store, to the loss by decline of temperature; and with an assigned density is proportional to the square of the linear dimensions. For small bodies it would be negli-

gible; for example, in the case of a planetoid a mile in diameter, composed of rock similar to the earth's surface strata and with  $a=2\times10^{-6}$ , it would be only two parts in a billion; but for a sphere having the same mass and dimensions as the earth, with the same value of a, it would be over one-fourth; in the latter case the treatment of the conduction of heat independently of its mechanical effects could hardly give more than a crude approximation. It seems conceivable that a planet considerably larger than the earth, even though practically solid, might exhibit the phenomenon described by Lane as occurring in gaseous bodies, of contraction accompanied by rise of temperature.

As compared, however, with the simple case just mentioned, there is an essential contrast shown with a distribution of temperature like that described above as characteristic of the mode of origin postulated by the planetesimal hypothesis. Here not only are the initial temperatures near the surface small in comparison with those developed in the interior, but the changes are widely different at different depths, the interior steadily shrinking as the heat is conducted outwards, while the outer strata tend at first to expand under the rise of temperature which continues until the maximum surface-gradient is reached. In the early stages the surface-gradient is slight; the thermal energy is for the most part simply redistributed within the earth, while comparatively little is lost through the surface. Thus any gain of heat from potential energy on the whole could come only through a preponderance of the internal shrinkage.

To estimate the nature of these movements let it be supposed that there is continual accommodation of the density of each portion of the mass to its temperature, while the accompanying variations of the pressure affecting a given particle are relatively negligible, so that there may be considered to be a definite coefficient of expansion a, a function of r.

If then  $\delta$  denote variations in time, the adjustment for equilibrium is determined by the conditions

$$\partial dv = a dv \partial \theta$$
  $\partial v = 4\pi r^2 \partial r$ 

where  $\partial r$  is the change in the central distance r of a given particle, so that

$$\delta v = 4\pi \int_{\bullet}^{\tau} a \, \delta \theta \, r^2 dr$$

The equation of expansion may also be written

$$\frac{\partial dv}{dv} = a\partial Q \qquad a = \frac{a}{aa}$$

in which a is in effect the coefficient of specific volume expansion referred to the variation in the heat content Q instead of the temperature  $\theta$ . Then the rate of radial motion is

$$\frac{\partial r}{\partial t} = \frac{1}{r^2} \int_0^r a \, \frac{\partial}{\partial r} \left( \lambda r^2 \, \frac{\partial \theta}{\partial r} \right) dr \tag{128}$$

by substitution of the value of  $\frac{\partial \theta}{\partial t}$  from the equation of conduction, while the total rate of work of gravity is

$$-\frac{d\theta}{dt} = -4\pi \int_{0}^{r_1} g\rho \, \frac{\partial r}{\partial t} \, r^2 dr \tag{129}$$

which by equation (3), through integration by parts, takes the alternative forms

$$-\frac{d\Phi}{dt} = -4\pi \int_{0}^{r_{1}} pa \frac{\partial}{\partial r} \left( \lambda r^{2} \frac{\partial \theta}{\partial r} \right) dr = 4\pi \int_{0}^{r_{1}} \lambda r^{2} \frac{\partial \theta}{\partial r} \frac{\partial (pa)}{\partial r} dr \qquad (130)$$

This gives simply the total rate at which energy is transformed from the potential form, while the manner of its localization remains undetermined. The last integral, which contains only thermodynamic quantities, suggests that the rate of transformation per unit volume might be  $\lambda \frac{\partial \theta}{\partial r} \frac{\partial (pa)}{\partial r}$ , but any such special interpretation is purely arbitrary as long as the thermodynamic substance is so incompletely defined.

The rates of specific linear expansion horizontally and vertically are

$$\varepsilon_1 = \frac{1}{r} \frac{\partial r}{\partial t} \qquad \varepsilon_2 = \frac{\partial}{\partial r} \left( \frac{\partial r}{\partial t} \right)$$
(131)

The sum of the latter and twice the former gives by (128) the rate of specific volume expansion  $a\frac{\partial \theta}{\partial t}$  as it should. The moment of inertia is

$$I = \frac{8}{3} \pi \int_{0}^{r_1} \rho r^4 dr$$
 (132)

and since  $\delta(\rho r^2 dr) = 0$  its variation is

$$\partial I = \frac{16}{3} \pi \int_{0}^{r_1} \rho r^3 \, \partial r \, dr$$

which gives

$$\frac{dI}{dt} = \frac{16}{3} \pi \int_{0}^{r_1} \rho r \, dr \int_{0}^{r} a \, \frac{\partial}{\partial r} \left( \lambda r^2 \, \frac{\partial \theta}{\partial r} \right) dr \tag{133}$$

Any supposition as to how a varies with the depth would appear to be wholly gratuitous, but it may be worth while to follow out a simple one suggested by the form of the equations, namely, that a is constant. Under this condition the radial motion is

$$\frac{\partial r}{\partial t} = a\lambda \frac{\partial \theta}{\partial r}$$

which is constantly negative at all depths, under all of the hypotheses entertained above in the computation of the temperature-curves, so that the

mass everywhere shrinks toward the center, even while the temperature is rising in the outer strata. In particular the surface falls at a rate proportional to the temperature-gradient there, so that its shrinkage is first accelerated and later retarded, the most rapid fall occurring when the zone of rising temperatures is disappearing.

In this case equations (131) become

$$\epsilon_1 = \frac{a\lambda}{r} \frac{\partial \theta}{\partial r}$$
 $\epsilon_2 = a \frac{\partial}{\partial r} \left( \lambda \frac{\partial \theta}{\partial r} \right)$ 

The former is everywhere negative; but the latter, if  $\lambda$  is constant, is negative where the temperature-curve is convex upward and positive where it is concave; moreover, where  $\epsilon_i$  is negative it is numerically less than  $\epsilon_i$ . Thus the adjustment of density to temperature demands, in the interior, both horizontal and vertical contraction, with the former more marked; in the superficial strata, as long as the temperature rises, horizontal contraction and vertical expansion. To the extent to which the mass resists deformation there are therefore developed at all depths a horizontal thrust and a vertical tension, which accumulate at rate proportional to  $\epsilon_2 - \epsilon_1$ ; this may be written

 $\epsilon_2 - \epsilon_1 = a\lambda r \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial \theta}{\partial r} \right)$ 

Numerical or graphic differentiation from the tabulated temperatures shows that at any one epoch the shearing stress thus indicated is roughly proportional to the square of the distance from the center.

The maximum possible shortening of the total radius, corresponding to a reduction of the temperature from its initial value  $\theta$  down to zero throughout the mass is

$$\varDelta r_1 = \frac{1}{r_1^2} \int_0^{r_1} a\theta r^2 \, dr$$

which reduces to

$$\Delta r_1 = \frac{a}{r_1^2 J} \int_0^T e \rho r^2 dr = \frac{aE}{4\pi J r_1^2}$$

The value of  $\partial r$ , between any two epochs can be found conveniently by comparison of this last integral with that coming from (128) integrated with respect to t by substitution of the appropriate value of  $\partial \theta$ . The computation shows that this total shortening, with  $\frac{a}{\sigma \rho}$  constant, would be something less than 10 per cent of the whole radius; and graphic integration from table 6 shows that about one-third of this would be accomplished during the epoch of rising temperatures, so that up to the time of maximum surface-gradient the circumference would diminish by about 800 miles. This number would, however, vary considerably under the different hypotheses, of which the one adopted for the moment is such as rather to exaggerate the influence of the shrinkage in the central parts, and unless the conductivity has been seriously underrated must probably be held to refer

to a period much longer than the whole of geological history. A measurement of the actual shortening indicated by the crumpling of the strata would allow an estimate of the length of time elapsed, or the "age of the earth." Near the beginning the shortening is roughly proportional to the square of the time, and as an indication of the order of magnitude a graphic integration from the same table gives about 100 miles in a billion years, the time being, moreover, inversely proportional to the numerical value used for the conductivity.

There remains to be considered what is perhaps the principal point of obscurity in the theory—the way in which the initial temperature is determined from the work of compression. This was done above through the supposition that between these two there existed a definite proportionality indicated by the specific heat, while the latter term was not sharply defined, but for numerical illustration was assigned the value 0.2, an average value of the ordinary specific heats of certain rocks. Now if e represent the work of compression per unit mass, the ratio  $\frac{de}{d\theta}$  for any path of compression is of the nature of a specific heat in physical dimensions, but its identification with  $\sigma$  in any definite sense of the latter (except of course that which might be defined as  $\frac{de}{d\theta}$  for the given path) amounts to a condition on the thermodynamic properties of the "working substance" whose import there is need to determine.

As concerns the relation of work and temperature, there may be considered to be two extreme cases conceivable, illustrated by the simple mechanical example of a weight in frictional contact with a horizontal plane and drawn by a spring. If the spring is very stiff it is only slightly extended, and the greater part of the work of the impressed force is done against the friction at the area of contact; if the spring is weak, the displacement of the point of application of the force comes largely from the extension of the spring and the corresponding work is stored as elastic

energy.

Corresponding to one extreme there is the fiction of a substance whose resistance to compression is purely frictional, its transformation of energy pure hysteresis—having at each density a certain critical pressure, the maximum it could sustain without further crushing, and as a function of the density to be used in formula (12) in computing the work of compression. Such a substance would show no tendency to restoration of volume on relief of pressure; and though the manner of transformation be obscure it seems natural to treat the heat derived from friction during compression as equivalent to heat obtained by conduction or radiation, so that the ratio of temperature to work would depend simply on the value, at the ultimate density, of the specific heat in nearly the ordinary sense as related to conduction at constant volume or constant pressure, at least if the coefficient of expansion be relatively small.

Such an interpretation read into Parts I and II would give a more definite and perhaps reasonably self-consistent theory; but the conditions described would fail to represent the behavior of surface-rock under the first moderate increments of pressure, and though they might be more closely followed under pressures beyond the observable crushing point, yet the agreement, for instance, of the theoretical and empirical values of the modulus of compression would be little more than coincidence.

The other extreme corresponds to what may be taken as the definition of a perfectly elastic substance in the thermodynamic sense, including for the present purpose not only fluids but perfectly elastic solids, since the work of shearing forces has been left out of account. Here the density depends in a definite way on temperature and pressure, independently of what series of changes the substance may have passed through; every path of change is strictly reversible, and in any closed cycle the excess of mechanical work is exactly accounted for by conduction and radiation, so that the work of adiabatic compression may be considered as stored elastic energy.

The actual materials composing the earth may be judged to partake to some extent of the properties of both extremes. Observed cases of the flowage of rocks would seem to be concerned chiefly with permanent change of shape, with little change of volume, but it is known that the equilibrium of a body as large as the earth could not be purely that of an elastic solid, unless it should possess elastic moduli much greater than those of known substances, so that most probably the violent pressures occurring even at moderate depths would lead to some permanent diminution of volume, or such as partly to persist in the event of removal of the pressure. On the other hand, direct experiments on the compressibility of rocks, under what must here be considered small ranges of pressure, show approximately perfect elasticity, with a relatively trivial amount of hysteresis.

It may well be that both extremes could represent acceptably the behavior of the same substance under different circumstances; for instance, according to the intervals of time involved. A bell made of pitch may sustain well-developed vibrations counted by hundreds per second and yet in a few hours flow into a permanently altered shape. Similarly the interior of the earth may be capable of sustaining seismic tremors and tidal oscillations like an elastic solid, and yet under steady and long-continued stresses yield in such a way that the expenditure of energy must be counted almost wholly dissipative.

Thus in view of the great length of time which must be assumed for the epoch of aggregation, the notion of compression with purely frictional resistance, accompanied by the production of permanent set or non-reversible diminution of volume, may be the appropriate one under the circumstances postulated by the planetesimal hypothesis, and would seem to demand no material modification in the essential features of the theory given in Parts I and II. For example, under a steadily progressive compression the pressure actually occurring with a given density at the corresponding depth would be at every epoch the critical pressure for that density, so that the density-curve for any epoch would necessarily, as was assumed without comment by Fisher, determine the path of compression traversed by a definite element of the mass.

It is likely that the phenomena of dynamical geology may themselves ultimately furnish the material for the most satisfactory estimation of the

properties of matter here in question. Their indication seems to point distinctly to the possibility of accumulation of truly elastic strains over periods of time much greater than those involved in the oscillatory movements commonly pointed to as witness to the existence of true elasticity. A reasonably complete theory would doubtless have to include the simultaneous contemplation of both elasticity and viscous plasticity, of volume and of shape, so as to complicate the theoretical deductions enormously.

To allow comparison it may, then, be of use for the present purpose to inquire what modifications are needed to give the previous theory the added definiteness which may come from a complete definition of the thermodynamic substance, but on the supposition that this possesses the opposite extreme property, of perfect elasticity of volume under all conditions. There remains, of course, the same possibility as before of variety in the secondary features; the following developments give in some detail a single form as illustration, one which has the advantage of relative simplicity in the analysis.

Let e now represent the total intrinsic energy per unit-mass; then a perfect fluid in the thermodynamic sense, or a substance which can do work only through hydrostatic pressure, and has perfect volume-elasticity in the sense described, finds its complete description conveniently in the analytic

form of p and e as functions of  $\theta$  and  $v = \frac{1}{\rho}$ . The condition of conservation of energy as embodied in the first law

$$dQ = \frac{\partial e}{\partial \theta} d\theta + \left( p + \frac{\partial e}{\partial v} \right) dv \tag{134}$$

gives the following determinations of auxiliary quantities

$$\sigma = \frac{\partial e}{\partial \theta} \qquad \sigma' = \sigma - \left(p + \frac{\partial e}{\partial v}\right) - \frac{\frac{\partial p}{\partial \theta}}{\frac{\partial p}{\partial v}} \qquad \kappa = \frac{\sigma'}{\sigma}$$
 (135)

where  $\sigma$ ,  $\sigma'$  are the specific heats, at constant volume and at constant pressure; also

$$K = -v \frac{\partial p}{\partial v} \qquad H = \kappa K \qquad a = \frac{\frac{\partial p}{\partial \theta}}{K}$$
 (136)  
the isothermal and isentropic bulk-moduli and a the co-

where K, H, are the isothermal and isentropic bulk-moduli and a the coefficient of volume-expansion. The existence of a definite entropy-function  $\epsilon$  imposes the condition of integrability

$$\frac{1}{\theta^2} \frac{\partial e}{\partial v} = \frac{\partial}{\partial \theta} \left( \frac{p}{\theta} \right) \tag{137}$$

in which case

$$\frac{\partial \epsilon}{\partial \theta} = \frac{\sigma}{\theta} \qquad \frac{\partial \epsilon}{\partial v} = \frac{\partial p}{\partial \theta} = Ka \qquad (138)$$

so that the condition of integrability is equivalent to

$$\frac{1}{\theta} \frac{\partial \sigma}{\partial v} = \frac{\partial (Ka)}{\partial \theta} \tag{139}$$

In addition to special hypotheses as to the form of the functions p,  $\epsilon$ , it would be necessary to specify the exact path of the compression in order to determine the rise of temperature produced by a given amount of mechanical work. It has, however, been assumed from the beginning that in view of the low conductivity of rock the compression might be considered as relatively instantaneous and therefore adiabatic; under this condition the path of compression would be a curve of constant entropy, and the ratio of mechanical work to rise of temperature would be determined by

$$\left(\frac{de}{d\theta}\right)_{\epsilon} = \frac{\partial e}{\partial \theta} \cdot \frac{p}{p + \frac{\partial e}{\partial n}}$$
 (140)

Comparison of this with (135) shows that  $\frac{de}{d\theta}$ , which was treated previously as a specific heat, can be identified with the specific heat at constant volume only at points where  $\frac{\partial e}{\partial v} = 0$ . This latter condition is satisfied identically by a perfect gas, which the substance might perhaps resemble in this respect, while differing widely in the relation between pressure, density, and temperature.

If, however,  $\frac{\partial e}{\partial v} = 0$  is satisfied everywhere, so that the intrinsic energy is a function of the temperature only, equation (137) shows that p would have the form  $p = \theta V$  and consequently by (136) that Ka = V; where V is some function of v only. Since at the surface the pressure vanishes, V would be zero for the argument  $v_1$ , hence the surface material would have to be either isothermally incompressible or have a zero coefficient of expansion. Now the observed compressibility and expansion of surface rock are enormously less than for gases, but the existence of an appreciable value for both of these is a necessary element in the application to dynamical geology, so that a correction is called for if the above be taken as the meaning of the specific heat used in equation (58). Though there is nothing to impose this special interpretation, the result still suggests one way in which a coherent theory can be constructed, as a modification of the previous one, but such as to take account of the measured values of all the thermal and dynamical coefficients.

Let it be supposed that the specific heat  $\sigma$  at constant volume is a constant, understood henceforth as measured in mechanical units; that the intrinsic energy, instead of depending on the temperature only, has the form

$$e = \sigma\theta + \varphi(v) \tag{141}$$

where  $\varphi(v)$  is a function of v to be determined; and that the isentropic lines have the form

 $p = f_1(\varepsilon) \frac{1}{v^2} + f_2(\varepsilon) \tag{142}$ 

The latter condition results from the Laplacian equation (21) by treating h and  $\rho_1$  as functions of the entropy, and is suggested as a condition in view of the assumption hitherto made, that the path of compression is deter-

mined by the relation between pressure and density as exhibited at various depths within the earth at any single epoch. For since the compression has been treated as adiabatic, this identification of the two thermodynamic paths means that as long as the effect of the conduction is insensible the nucleus would be in a condition of isentropic or convective equilibrium such as described by Ritter and Kelvin. The generalization of equation (21) consists in supposing that it would give the form of the pressure-density curve corresponding to convective equilibrium for any value of the entropy by proper choice of the constants h and  $\rho_1$ . It is, then, required to determine the functions  $f_1, f_2, \varphi$ , so as to satisfy the given conditions. Equation (134) shows that

$$ds = \frac{\sigma}{\theta} d\theta + \frac{p + \varphi'}{\theta} dv \tag{143}$$

in which the coefficient of dv must therefore be a function of v only, which for convenience may be written

$$\frac{p + \varphi'(v)}{\theta} = \sigma \cdot \frac{\psi'(v)}{\psi(v)} \tag{144}$$

and then the integral of (143) is

$$\theta \psi = \zeta = e^{\frac{\epsilon}{\sigma}}$$
 (e = Naperian base) (145)

in which the constant of integration is considered to be absorbed in the undetermined function  $\phi$ .

Elimination of  $\theta$  from (144) and (145) gives

$$p = \sigma \zeta \frac{\psi'}{\dot{\psi}^2} - \varphi' \tag{146}$$

which must be identical with (142), and thus gives

$$\sigma\zeta\frac{\dot{\psi}'}{d\dot{z}} - \varphi' = \frac{f_1(\epsilon)}{n^2} + f_2(\epsilon)$$

Hence

$$f_1(\epsilon) = \sigma A \zeta + a$$
  $f_2(\epsilon) = -\sigma B \zeta - b$  (147)

and

$$\frac{\psi'}{d^2} = \frac{A}{v^2} - B \qquad \qquad \varphi' = -\frac{a}{v^2} + b$$

from which come

$$\psi = \left(\frac{A}{v} + Bv + C\right)^{-1} \tag{148}$$

$$\varphi = \frac{a}{v} + bv \tag{149}$$

The constant of integration in  $\varphi$  is omitted, since only differences in the intrinsic energy are in question, so that there remain five undetermined constants. In terms of these auxiliary functions, then, the properties of the substance are described by equations (141), (144), and (145), from which may be deduced the following:

$$-\frac{K}{v} = \frac{\phi \phi'' - \phi'^2}{\phi^2} \cdot \sigma \theta - \varphi'' \tag{150}$$

$$Ka = \sigma \frac{\psi'}{\phi} \qquad H = \frac{2}{\sigma^2} (\sigma A \zeta + a)$$

$$\kappa = 1 + \frac{Kv \theta a^2}{\sigma}$$
(151)

$$\kappa = 1 + \frac{Kv\theta a^3}{a} \tag{152}$$

Since the pressure-density curve at the close of the epoch of compression is supposed to be an adiabatic line, the variation at different depths of all the magnitudes concerned, for a planet of definite mass, will be determined in terms of the constants introduced, when a value is assigned for the entropy, which may as well be taken equal to zero, since the level of reckoning is arbitrary. The various surface-values are then fixed by the condition  $p_1 = 0$ , with  $\epsilon_1 = 0$ , so that the constants are subject to the conditions:

$$v_1^2 = \frac{\sigma A + a}{\sigma B + b} \tag{158}$$

$$\theta_1 = \frac{A}{v_1} + Bv_1 + C \tag{154}$$

$$\frac{K_1 a_1 \theta_1}{\sigma} = \frac{A}{\mathfrak{v}_1^2} - B \tag{155}$$

$$\frac{H_1}{2} = \sigma B + b \tag{156}$$

If then  $K_{\nu}$ ,  $v_{\nu}$ ,  $\theta_{\nu}$ ,  $a_{\nu}$ ,  $\sigma_{i}$  are considered to be obtained by direct measurement,  $\sigma$  and  $H_{1}$  may be computed from

$$\sigma = \sigma_1' - K_1 v_1 \theta_1 a_1^2 \tag{157}$$

$$H_{1} = K_{1} \left\{ 1 + \frac{K_{1}v_{1}\theta_{1}a_{1}^{2}}{\sigma} \right\}$$
 (158)

and then the solution of (153) to (156) gives

$$B = \frac{A}{v_1^2} - \frac{K_1 a_1 \theta_1}{\sigma} \tag{159}$$

$$a = \frac{H_1 v_1^2}{2} - \sigma A \tag{160}$$

$$b = \frac{H_1}{2} - \sigma B \tag{161}$$

$$C = \theta_1 - \frac{A}{v_*} - Bv_1 \tag{162}$$

leaving the single parameter A undetermined. The Laplacian constant h is  $h = H_1 v_1^2$ (163)

in terms of which the distribution of pressure and density are still given by (21) and (25), while the excess of intrinsic energy and of temperature over their surface-values are

$$e - e_1 = \frac{H_1}{2} \frac{(v_1 - v)^2}{v} \tag{164}$$

$$\theta - \theta_1 = \frac{A}{vv^2} (v_1 - v)^2 + \frac{K_1 a_1 \theta_1}{\sigma} (v_1 - v)$$
 (165)

the former corresponding exactly to (22) above.

In the equation (165) for the temperature the first term corresponds, except as to the value of the coefficient, to that which alone occurred in the analogous equation in Part I for the case of constant specific heat; while the second term is new and may be considered as the corrective term needed to take account of the coefficient of expansion, which occurs as one of its factors. The numerical value however of this corrective term is small; for instance, with  $K_1=4\times 10^{11}$ ,  $\theta_1=300$  (the absolute temperature of the surface),  $a_1=2\times 10^{-6}$  and  $\sigma=\frac{1}{5}J$ , its maximum value, which occurs at the center where the density is greatest, is about 80°, while it contributes an initial surface gradient of 1° in 14,000 meters. The value here used for  $K_1$  comes by comparison with the value deduced for  $H_1$  in Part I, which, as is seen by (158), exceeds it by only one four-hundredth part and is known to range well with the results of direct measurement on surface rock.

It appears thus that to take account of all the measured mechanicalthermal constants relating to surface-rock it is sufficient to include only this trivial variation from the distribution of temperature specified by the first term of (165), which in algebraic form is identical with that occurring in the corresponding case in Part I. But the absolute value of this principal term depends on the coefficient A, which is here left undetermined, instead of having the definite value  $h/2\sigma$  as under the former hypothesis. So far as concerns consistency with the conditions thus far assumed, this constant might be chosen so as to give any assigned value to the central temperature for example, or to the surface-gradient at some particular epoch of the conduction. But to make even the maximum surface-gradient match the present observed value of 1° in 30 meters it would be necessary to choose A so that the initial temperatures, while similar in relative magnitude at the various depths, would be in absolute value several times as large as those listed in column 8 of table 2. This would perhaps be a rather extreme supposition, though there seem to be no definite data to the contrary.

A suggestion from another source as to a fair mean value to be taken for A is the following:

In the assumed expression (141) there are the two terms:  $\sigma\theta$ , which may be considered for vividness as the kinetic portion, and  $\varphi(v)$  the potential portion, of the intrinsic energy e. The latter part, depending conceivably simply upon the mutual distances of the constituent particles, may by analogy with the dynamics of particles plausibly be supposed always to increase as v increases. Now from (149), transformed by substitution of the constants as determined in terms of the surface-data, comes

$$\varphi'(v) = \left(\sigma A - \frac{H_1 v_1^2}{2}\right) \left(\frac{1}{v^2} - \frac{1}{v_1^2}\right) + K_1 a_1 \theta_1 \tag{166}$$

so that as v decreases from the value  $v_i$ , the sign of  $\varphi'$  is ultimately that of  $\sigma A = \frac{H_1 v_1^2}{2}$ , unless this be zero. If then  $\varphi$  is to be an increasing function of v, the most moderate value of A which can be assumed is

$$A = \frac{H_1 v_1^2}{2\sigma} = \frac{h}{2\sigma} \tag{167}$$

which as appears from (22) and (58) would give from the first term of (163) a temperature distribution precisely the same also in absolute values as that deduced under the first hypothesis in Part I.

This result shows that there is not necessarily any radical difference between the temperature-distributions deducible from the two alternative extreme suppositions described, though variations in the special hypotheses may be expected to produce here, as under the opposite view, considerable differences in the quantitative conclusions.

It has been pointed out that the surface-gradient of temperature as deduced from the theory would probably never reach the value at present found by observation, at least unless the conductivity increase considerably from the surface downward. But the present theory has taken account only of the heat obtained from gravitational energy, to which must be added that obtained from several other assignable sources. These might be relatively unimportant, so that their effect could be included in the sense of corrections to the above results; but if of sufficient magnitude they might alter the features of the thermal process completely.

In particular, if heat were steadily generated in each unit of volume at rate  $\varphi(r)$ , the equation of conduction would be

$$\sigma \rho \frac{\partial \theta}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( \lambda r^2 \frac{\partial \theta}{\partial r} \right) + \varphi(r)$$
 (168)

the solution of which may be written

$$\theta = u + \int_{r}^{r_1} \frac{dr}{\lambda r^2} \int_{0}^{r} r^2 \varphi(r) dr$$
 (169)

where u satisfies the equation

$$\sigma \rho \frac{\partial u}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( \lambda r^2 \frac{\partial u}{\partial r} \right)$$

and is to be determined so that  $\theta$  satisfies the given initial and boundary conditions. For example, if  $\varphi$  is constant or the rate of generation per unit volume the same throughout the mass, the steady component, defined by the integral in (169), is, with  $\lambda$  constant:

$$\theta = \frac{\varphi}{6\lambda}(r_1^2 - r^2)$$

whence

$$\theta = \frac{\varphi}{6\lambda} (r_1^2 - r^2)$$

$$\gamma_1 = \frac{\varphi r_1}{3\lambda} \qquad \theta_0 = \frac{\varphi r_1^2}{6\lambda} \qquad \frac{\theta_0}{\gamma_1} = \frac{r_1}{2}$$

so that with the flux corresponding to thermal equilibrium a surface gradient of 1° in 30 meters would mean a central temperature of 100,000°, whatever be the values of specific heat and conductivity. An effect of such magnitude, produced by radio-activity or otherwise, is not to be lightly assumed. It is perhaps more likely that the effect of these agencies is largely confined to the superficial strata.

Another possible explanation of the discrepancy respecting the temperature-gradient is that the assumed density laws may not properly represent the variation of density near the surface. For, independently of any special hypothesis, it is plain that in descending from the surface the density would tend to increase on account of the increase of pressure, and to decrease by virtue of the increase in temperature; which effect controls depends on the values of elastic modulus, coefficient of expansion, and thermal gradient.

Let the density  $\rho$  through its dependence on p and  $\theta$  be thereby a function of the distance s below the surface. Then

$$\frac{d\rho}{ds} = \frac{\partial\rho}{\partial p} \frac{dp}{ds} + \frac{\partial\rho}{\partial\theta} \frac{d\theta}{ds}$$

but since

$$\frac{dp}{ds} = g\rho \quad , \quad \frac{\partial \rho}{\partial p} = \frac{\rho}{K}$$

$$\frac{d\theta}{ds} = \gamma \quad , \quad \frac{\partial \rho}{\partial \theta} = -a\rho$$

this may be written:

$$\frac{d\rho}{ds} = \frac{\rho}{K} (g\rho - Ka\gamma) \tag{170}$$

With the values  $K=4\times10^{11}$ ,  $a=2\times10^{-4}$  used above, which appear to be well supported by observation, this would be positive or negative according to whether the gradient is less than or more than 1° in 30 meters, or just about the observed value. If the gradient were greater than this there would be at first an actual decrease of density from the surface downward, because of the preponderant effect of temperature over pressure; if less there would be an immediate increase in density such as is implied in the formulas (25) and (74). In the intermediate case, where  $Ka\gamma = g\rho$ , as appears to be nearly realized at the present time, the density-curve would have a horizontal tangent at the surface-point. It would be useful if a family of such density-curves could be found, expressible in tractable analytic form, and satisfying the conditions named in connection with equation (92), so that the effect of such a modification could be determined, through a review of the preceding theory with the appropriate changes.

For a discussion of the bearing of these results on geological theory, reference must be made to the papers of Professor Chamberlin, to whom the writer is deeply indebted, not only for the opportunity of co-operation in this work, but for suggestion and assistance freely given during repeated conferences.



CONTRIBUTIONS TO	COSMOGONY	AND THE	FUNDAMENTAL	PROBLEMS OF	GEOLOGY
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THE RELATIONS OF EQUILIBRIUM BETWEEN THE CARBON DIOXIDE OF THE ATMOSPHERE AND THE CALCIUM SULPHATE, CALCIUM CARBONATE, AND CALCIUM BICARBONATE OF WATER SOLUTIONS IN CONTACT WITH IT

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# THE RELATIONS OF EQUILIBRIUM BETWEEN THE CARBON DIOXIDE OF THE ATMOSPHERE AND THE CALCIUM SULPHATE, CALCIUM CARBONATE, AND CALCIUM BICARBONATE OF WATER SOLUTIONS IN CONTACT WITH IT.

When two difficultly soluble salts, such as barium sulphate and barium carbonate, are formed in a given medium, for instance by the addition of barium chloride to a mixture of potassium sulphate and carbonate, they are precipitated, as is well known, in the order of their insolubility. In the given case barium sulphate, the less soluble salt, is precipitated first, the more soluble carbonate last. We apply this principle in the familiar case of the volumetric determination of chlorides by titration with silver nitrate, in which potassium chromate is used as indicator; silver chromate is very difficultly soluble, but silver chloride is less so, and is precipitated almost completely and within the limits of exact quantitative analysis, before any solid red silver chromate can permanently be formed, the first persisting appearance of the latter being taken, indeed, as the evidence or indication that the precipitation of the chloride has just been completed.

The application of the laws of physical chemistry, especially those of chemical and physical equilibrium, to such cases of precipitation shows, however, that there must be a limit to this principle of the order of precipitation; the principle itself may be derived by the application of these laws and is always, of course, subject to them. The existence of such a limit and its relations to the solutions in contact with given salts have been investigated experimentally in a number of cases, the most notable investigation being the classical one of Guldberg and Waage <sup>1</sup> on the conditions of equilibrium between barium sulphate and carbonate, and potassium sulphate and carbonate. The limiting values in all such cases are of extreme interest, as from them certain definite conclusions may be drawn as to the nature of precipitates formed in given cases; or, vice versa, from the nature of the precipitate, conclusions as to the composition of the medium may be drawn, and the existence of a limiting value leads to the possibility of a complete reversal of the usual order of precipitation under given conditions.

As has just been mentioned, and as will be shown in detail presently, the limiting value is for two given, little-soluble salts most intimately associated with the composition of the liquid medium from which precipitation occurs; the composition of the medium may in turn be dependent for one or more of its essential components, e.g., dissolved carbonic acid, on the nature of the atmosphere above the solution, with the result that the composition of the atmosphere may become a function in the mathematical expressions deduced by the application of the laws of physical chemistry to the facts of precipitation.

<sup>&</sup>lt;sup>1</sup> Journal für Praktische Chemie (2), 19, 69 (1879).

Considerations of this nature led the author in 1903,1 in the course of a conversation with Dr. T. C. Chamberlin on the remarkable freedom from calcium carbonate of a deposit of gypsum,2 to suggest that possibly there might be some connection between the purity of the gypsum and the carbon dioxide content of the air at the period of the gypsum formation, since the carbon dioxide in the atmosphere is one of the most important factors influencing the solubility of calcium carbonate.

Inasmuch as climatic conditions, according to recent theories entertained qualifiedly by Dr. Chamberlin, are also dependent to a certain degree on the carbon dioxide in the atmosphere, it seemed possible that a study of the precipitation of calcium sulphate and calcium carbonate from the point of view of the laws of equilibrium might lead to conclusions which would be of some use as a further source of information relative to conditions existing at a remote period.

Partly on account of the possibility of obtaining results of some such specific geological value for the work on the climates of the earth; chiefly, however, in order to test the possibility of exploiting this method of investigation for geological purposes, Dr. Chamberlin asked me to undertake, in collaboration with himself, the work of making the necessary calculations on the conditions of equilibrium determining the precipitation of calcium sulphate and calcium carbonate.

As is usual in these cases, it was decided to consider first the ideal case of solutions containing only the two salts in question. But the work has been extended to estimate proximately the influence of the presence of other sulphates in the solutions in the proportions found in ocean waters of the present day; and finally an attempt has been made to consider the effect of concentrated salt (sodium chloride) solutions on the conditions The results obtained for the simpler case of equilibrium for dilute studied. solutions in the presence of sulphates and moderate amounts of sodium chloride may, it is hoped, also prove useful in connection with present-day problems on the calcium carbonate content of the oceans and of fresh waters.

The study of the equilibrium conditions controlling the precipitation of calcium carbonate and sulphate falls naturally into two parts—a study, on the one hand, of their relative solubilities, and the consideration, on the other hand, of the conditions of equilibrium for saturated solutions of calcium carbonate, calcium bicarbonate, and carbonic acid in equilibrium with an atmosphere of some given content of carbon dioxide, the latter being a determining factor in the total solubility of carbonate. This second and more complex part of the study will be taken up first.

Year Book No. 2, Carnegie Institution of Washington, p. 269.
 The observation was made by Mr. F. A. Wilder in the course of an investigation for a doctor's thesis submitted to Professor Chamberlin.
 Pressure of other work made it necessary to postpone the calculations to the year 1907

EQUILIBRIUM IN AQUEOUS SOLUTIONS OF CALCIUM CARBONATE. CALCIUM BICARBONATE, AND CARBONIC ACID IN CONTACT WITH AN ATMOSPHERE CONTAINING CARBON DIOXIDE, AND THE SOL-UBILITY OF CALCIUM CARBONATE IN WATER CONTAINING FREE CARBONIC ACID.

The most reliable and complete experimental determinations of the solubility of calcium carbonate in water containing free carbonic acid were made by Schloesing.1 The theoretical treatment of his results from the point of view of equilibrium conditions we owe to Bodlaender.<sup>2</sup> The latter's work, correct in its theoretical treatment,<sup>2</sup> shows an error of moment in the calculation of the solubility constant of calcium carbonate, the constant most important to us, an error due largely to an error in one of the investigations from which Bodlaender drew his data.4 McCoy's more recent work on the equilibrium in aqueous solution for sodium carbonate, sodium bicarbonate, and carbonic acids gives the necessary material for the correction of the above error in the following pages.

The complex conditions of equilibrium involved when water is saturated with calcium carbonate and with carbon dioxide under any given partial pressure may be developed as follows: For a saturated solution of calcium carbonate, say in contact with the solid carbonate, we have

$$\underline{\text{CaCO}_{3}} \leftrightharpoons \text{CaCO}_{3} \tag{1}^{7}$$

Calcium carbonate in aqueous solution is very largely ionized according to  $CaCO_{\bullet} = Ca'' + CO_{\bullet}''$ 

At a given temperature in a saturated solution of a difficultly soluble salt of this nature the product of the concentrations of the ions is a constant,\* which is called the solubility product or the ion product of the salt:

$$C_{\text{Ca}} \times C_{\text{CO}_2} = K_{\text{CaCO}_2} \tag{3}$$

That the product of the ion concentrations is equal to a constant for saturated solutions of difficultly soluble salts must at present be considered an empirically established fact. As is well known, the law of mass-action does not give constants when applied to the ionization of strong electrolytes, such as salts are. For instance, for the reversible reaction

$$NaCl = Na' + Cl'$$
 (4)

\* Ibidem.
\* Underscoring of a symbol is used to indicate that the substance is in solid form.
\* See below in regard to the conclusion usually based on this equation that at a given temperature the concentration of the dissolved non-ionised calcium carbonate molecules, CaCO<sub>3</sub>, or the molecular solubility, has a constant value.
\* The term concentration, for which C is used in all the equations, is taken, in accord with chemical practice, to designate the number of gram molecules or moles of substance in 1 liter of a solution or of a gas.
\* Ostwald, Scientific Foundations of Analytical Chemistry; Nernst, Theoretical Chemistry, p. 531 (1904); Bodlaender, loc. cit.; A. A. Noyes, Zeitschrift für Physikalische Chemie, 16, 125 (1895), 26, 152 (1898), 42, 336 (1902); Report of the Congress of Arts and Science, vol. IV, 322 (1904); Le Blanc, Zeitschrift für Anorganische Chemie, 51, 181 (1906).

<sup>&</sup>lt;sup>1</sup> Comptes Rendus, 74, 1552 (1872); 75, 70 (1872).

<sup>2</sup> Zeitschrift für Physikalische Chemie, 35, 23 (1900).

<sup>3</sup> See below, this page, in regard to a contested question

<sup>4</sup> McCoy, American Chemical Journal, 29, 437 (1903).

<sup>5</sup> Thidam ition of theory.

we find as a matter of experience that the proportion

$$\frac{C_{Na} \times C_{Cl}}{C_{NaCl}} \tag{5}$$

is not a constant for different concentrations, as the corresponding expression is for all other kinds of reversible reactions, including the ionization of weak bases and weak acids. The above proportion for a strong electrolyte grows larger with increasing concentration—the most promising explanation of this apparently abnormal behavior being perhaps that the ionizing power of the solution is changed by the presence of considerable numbers of ions (the "salt-effect" of Arrhenius).

This result, applied to the ionization of calcium carbonate (equation 2), would mean that the proportion

$$\frac{C_{C_b} \times C_{CO_b}}{C_{C_b \cap CO_b}} \tag{6}$$

is not a constant.

It is ordinarily assumed that for the saturated solutions of difficulty soluble salts the molecular concentration of the salt (here  $C_{O_0O_0}$ ) is a constant at a given temperature in all aqueous solutions: we would expect then, from what has just been said, that the product  $C_{O_0} \times C_{O_0O_0}$  could not have a constant value, since it is the numerator in the variable proportion (6). As a matter of experiment, however, A. A. Noyes, Findlay, and others found in a number of carefully studied cases of similar salts that the solubility products are constants, whether the given salt is present alone or in the presence of another salt modifying its ionization, such as a salt with an ion in common with it.

The peculiar discrepancy between the empirical results expressed in (5) and (6) on the one hand, and the empirical result expressed in the constancy of the ion product on the other hand, as just explained, seems to find a satisfactory explanation in the work of Arrhenius on the solubility of salts in salt solutions.<sup>1</sup>

Arrhenius shows that the old view must be abandoned that in the presence of excess of the solid salt, the solubility of the molecular or non-ionized salt is a constant in different saturated solutions (i.e., in solutions saturated in the presence of other salts). His experiments on the solubility of the silver salts of various organic acids (silver acetate, valerate, etc.) in the presence of varying amounts of the sodium salts of the same acids show that the solubility of the non-ionized silver salt grows smaller with increased concentration of the sodium salt present. In other words, there is no constant molecular solubility of a precipitate, as has so long been assumed. The case is analogous to the decreased solubility of gases, such as oxygen or carbon dioxide, in salt solutions as compared with pure water—a fact which is used below in the discussion of the equilibrium conditions.

Arrhenius uses his data as an argument against the correctness of some of Noyes's conclusions. No attempt, however, seems to have been made by Arrhenius in this paper to study the ion-products for the silver salts in his own experiments, and calculations were therefore made with his material to

<sup>&</sup>lt;sup>1</sup> Zeitschrift für Physikalische Chemie, 31, 221 (1899).

ascertain whether, in spite of (or rather because of) the variability of the molecular solubilities, the silver salts give constant solubility products or not. As is seen from the tables given below, the extremely interesting result was obtained that, according to Arrhenius's own experiments, the silver salts, whether present alone or with varying amounts of sodium salts with the acid ion in common with them, give rather good constants for the solubility products.

As the question of the constancy of the solubility or ion product for a difficultly soluble salt is of particular importance in the investigation this paper treats of, space will be taken here to report the calculations made with Arrhenius's data for three of the silver salts, the acetate, which is the most soluble salt studied, the valerate, and the butyrate, which are very much less soluble than the acetate.

In table 1, giving the solubility of silver acetate at 18.6° in the presence of varying amounts of sodium acetate, column 1 gives the molar concentration of sodium acetate used; column 2 gives the degree of ionization of the sodium acetate in the mixture; column 3 gives the concentration of the ionized sodium acetate; column 4 the total solubility of silver acetate; column 5 the degree of ionization of the silver acetate; column 6 the concentration of the ionized part of the silver acetate; column 7 the concentration of the non-ionized part, which represents therefore the molecular solubility of the silver salt. Columns 1, 4, 5, 6, 7 are taken from Arrhenius's tables; the degrees of ionization of the sodium acetate as given in column 2 were calculated with the aid of the isohydric principle, whose reliability has been amply demonstrated.¹ Column 3 is derived from columns 1 and 2.

For a saturated solution of silver acetate

$$CH_{2}CO_{2}Ag = CH_{2}CO_{2}' + Ag'$$
 (7)

the solubility product would be

$$C_{Ag} \times C_{CH_sCO_s} = K \tag{8}$$

in which  $C_{CH_2CO_2}$  represents the total concentration of acetate ions irrespective of their origin from silver or sodium acetate; in each of the experiments it is the sum of the values given in a line under columns 3 and 6. The values of the solubility product constant K, as calculated, are given in the last column.

1	2	8	4	5	6	7	8
Na-Acet.	100-1	10 <sup>8</sup> Acet.'	Ag-Acet.	100ag	10º Acet."	10º Mol.	K×10
0			0.0593	72.0	42.7	16.6	182
0.0333	80.0	26.6	0.0474	68.1	32.3	15.1	190
0.0667	78.0	52.0	0.0384	64.4	24.7	13.7	190
0.1333	75.0	100.0	0.0282	58.4	16.4	11.8	191
0.2667	69.6	186.7	0.0203	50.4	10.2	10.1	200
0.5000	63.0	315.0	0.0147	42.8	6.3	8.4	202

TABLE 1 .- Silver Acetate.

<sup>&</sup>lt;sup>1</sup> Noyes, Congress of Arts and Science, St. Louis, vol. IV, p. 318, gives an excellent summary on this question.

Tables 2 and 3 correspond to table 1.

TABLE 2.—Silver Valerate.

1	2	8	4	5	6	7	8
Na-Val.	100a <sub>1</sub>	10° Val.	Ag-Val.	100ag	10° Val."	10° Mol.	K×104
0 0.0175 0.0349 0.0689 0.1395	86.5 84.0 80.1 75.8	15.1 29.3 55.9 105.7	0.0095 0.0047 0.0030 0.0018 0.0015	87.3 81.1 75.5 68.1 59.7	8.3 3.8 2.2 1.2 0.9	1.2 0.9 0.8 0.6 0.6	6.9 7.2 6.9 6.9 (9.6)

TABLE 3.—Silver Butyrate.

1	2	8	4	5	6	7	8
Na-Butyr.	100a <sub>1</sub>	10 <sup>a</sup> Butyr.	Ag-Butyr.	100a <sub>2</sub>	10° Butyr.	10° Mol.	K×10 <sup>8</sup>
0 0.0066	86.0	56.8	0.0224 0.0199	81.1 79.6	18.2 15.8	4.2 4.1	33.0 (49.8)
0.0164	84.9	13.9	0.0169	77.3	13.1	3.8	35.4
0.0329	83.0	27.3	0.0131	73.5	9.6	3.5	35.4
0.0658	80.0	52.6	0.0091	67.7	6.2	2.9	36.4
0.1315	75.9	100.0	0.0060	59.9	3.6	2.4	37.3
0.2630	70.1	184.4	0.0040	51.1	2.0	2.0	36.8
0.4930	63.3	312.1	0.0027	43.2	1.2	1.5	37.6

It is quite obvious from a consideration of the values in the last column of each table that rather satisfactory constants are obtained in all cases for the ion products of the silver salts in saturated solutions. It may be added that of the two bracketed irregular values, the one in table 2 (last line) corresponds to an experiment which shows the probability of some experimental or other error in considering the seventh (next to the last) column, where 0.6 remains unchanged, while it should grow smaller. And the irregular value in table 3 (line 2) corresponds to an experiment the figures for which, as given by Arrhenius, show a decided divergence from the principle of isohydric solutions—so that it also is unreliable.

Since, then, the results of Arrehnius's determinations, as thus calculated, agree with the conception that for a difficultly soluble salt the solubility product is a constant at a given temperature for saturated solutions, and since this conclusion was also reached experimentally by A. A. Noyes, Findlay, and others, as explained above, we may accept this now as an empirically-established fact. The values calculated below for the solubility product of calcium carbonate on the basis of Schloesing's data also show excellent agreement.<sup>1</sup>

The value of the "solubility product" for calcium carbonate is particularly important for the study of the precipitation of calcium carbonate under varying conditions, and its calculation is one of the first objects of this investigation. Its significance lies in the fact that since in saturated solutions of calcium carbonate in different mixtures the concentrations of the calcium and the carbonate ions are variable, they need not and usually

<sup>&</sup>lt;sup>1</sup> Vide Stieglitz, Journal of the American Chemical Society, 30, 946 (1908), for a more complete discussion of this question.

would not have equal values, but they are dependent on each other to the extent that the product of the two concentrations has a constant value for the saturated solutions. For instance, if to a saturated solution of the carbonate any acid is added, either a strong one like hydrochloric acid or a weak one like carbonic acid, the hydrogen ions of the acid must immediately combine to some extent with part of the carbonate ions, CO<sub>3</sub>", to form more or less bicarbonate ions, HCO<sub>3</sub>': as the CO<sub>3</sub>" ions disappear, more molecular calcium carbonate must ionize (equation 2) to re-establish the equilibrium, leaving the solution undersaturated with molecular carbonate, and the solid carbonate, if present, must dissolve. All this can be briefly expressed in the equation

$$C_{\text{Ca}} \times (C_{\text{CO}_3}"-x) < K_{\text{CaCO}_3}$$
 (9)

The solution is undersaturated when the product of the concentrations of the calcium and carbonate ions is smaller than the solubility constant; similarly oversaturated (precipitation resulting) when the product is greater than the constant; and just saturated when the product equals the constant.

When the solubility of calcium carbonate is thus increased by the addition of an acid (say carbonic acid) owing to the formation of bicarbonate ions, HCO<sub>4</sub>, calcium bicarbonate Ca(HCO<sub>2</sub>), is formed; it remains, as most salts do in dilute solutions, very largely ionized. In equations (3), etc., C<sub>Ca</sub> means, of course, the total concentration of calcium ions, irrespective of their origin from calcium carbonate or bicarbonate.

These relations which we have been discussing in a qualitative sense may be developed quantitatively as follows:

The formation of calcium bicarbonate by the action of carbonic acid on calcium carbonate is a reversible reaction:

$$Ca'' + CO_{\underline{a}}'' + H' + HCO_{\underline{a}}' = Ca'' + 2HCO_{\underline{a}}'$$
(10)

and

$$Ca'' + 2HCO_a' = Ca(HCO_a)_a \tag{11}$$

The calcium ions appearing on both sides of equation (10) in equal quantities evidently do not affect the equilibrium, and we have more simply

$$CO_a'' + H \cdot + HCO_a' = 2HCO_a''$$
 (12)

and consequently:

$$C_{\text{CO}_a} \times C_{\text{H}} \times C_{\text{HCO}_a} = k \times C_{\text{HCO}_a}$$
 (13)

Canceling C<sub>HCO<sub>4</sub></sub> on both sides, we have

$$\frac{C_{CO_3} \times C_H}{C_{HCO_3}} = K''_{Ionisation}$$
 (14)

The study of these equations shows that, except for the formation of some non-ionized calcium bicarbonate, the formation of bicarbonate and the equilibrium between bicarbonate and carbonate are largely independent of the nature of the metal ion present, particularly since all salts (like calcium bicarbonate) are largely ionized in dilute solutions and all similar salts are about equally ionized in equivalent solutions. The above conclusion has

been confirmed by the work of Bodlaender on calcium and barium bicarbonate and of McCoy on sodium bicarbonate.

Equation 14 represents the equilibrium condition between carbonate ions, hydrogen ions, and bicarbonate ions, or the secondary ionisation of carbonic acid expressed in  $HCO_{a}' = H \cdot + CO_{a}''$ 

and the constant of the equation may be called the second ionization constant of this acid.

The primary ionization of carbonic acid, which must supply the major portion of hydrogen ions, is expressed in

$$H_2CO_2 = H \cdot + HCO_2' \tag{16}$$

and we have then:

$$\frac{C_{H} \times C_{HCO_{2}}}{C_{HcO_{2}}} = K'_{Ionisation}$$
 (17)

K'Ionization may, then, be called the first ionization constant of carbonic acid.

The concentration of carbonic acid in solution is, according to Henry's law, at a given temperature, proportionate to the concentration or partial pressure of the gaseous carbon dioxide in the atmosphere with which the solution is in equilibrium, viz:

$$C_{\text{H}_2\text{CO}_3} = k_{\text{gas}} \times C_{\text{CO}_3} \tag{18}$$

This completes the equations involved in the complex condition of equilibrium we are considering. Summarizing our conclusions, we have the following four mathematical equations expressing the conditions of equilibrium in saturated solutions of calcium carbonate and bicarbonate in contact with the atmosphere, all the constants of which must be simultaneously fulfilled for the condition of equilibrium:

$$\begin{array}{lll} I^1 & C_{CO_3} \times C_{CO_3} = K_{Solub. \ Prod.} \\ II^2 & C_{H_2CO_3} = k_{gas} \times C_{CO_2} \\ III^3 & C_H \times C_{HCO_3} = K'_{Ionisation} \times C_{H_2CO_3} \\ IV^4 & C_H \times C_{CO_3} = K''_{Ionisation} \times C_{HCO_3} \end{array}$$

The solubility of calcium carbonate, either as carbonate or as bicarbonate, reaches a limit when the solubility product of equation I is reached, and the value  $C_{CO_0}$ , the concentration of the carbonate ions, in this equation is in turn a function of equation IV; two values of this equation are functions of equation III, in which in turn the concentration of the dissolved carbonic acid C<sub>H,CO</sub>, is dependent on the atmospheric carbon dioxide as expressed in equation II.

The constants of equations II, III, and IV are known, and the constant of equation I, which we wish to determine, can be obtained from the other constants with the aid of Schloesing's experimental work on the solubility of calcium carbonate.

The solubility product of a saturated solution.
 The solubility of carbon dioxide under varying partial pressures.
 The primary ionization of carbonic acid.
 The secondary ionization of carbonic acid.

The solubility factor of carbon dioxide in water,  $k_{\rm max}$  of equation II, has been determined by Bunsen¹ for different temperatures. The solubility is usually given in liters (a) of gas, reduced to 0° and 760 mm., absorbed by 1 liter of water; then to reduce this to terms of gram molecular concentrations as required for the application of the mass-action law, we make

$$k_{\rm gas} = \frac{a}{22.4} \tag{19}$$

since a gram molecule of a gas occupies 22.4 liters under normal conditions. For instance, at 16°, 0.9753 liter is absorbed or 0.9753/22.4 = 0.04354 mole, if the carbon-dioxide gas has the pressure of 1 atmosphere. For any other pressure P of the gas, expressed in atmospheres, the molar concentration of dissolved carbonic acid is, then, according to II

$$C_{H_{cOO_3}} = k_{gas} \times P \tag{20}$$

In salt solutions the solubility is considerably less than in pure water, as determined by Setchenow and more recently by Geffcken, and, when salts are present, corrections made on the basis of these determinations will be used.

The first ionization constant of carbonic acid (equation III) has been determined by Walker and Cornacks from the conductivity of aqueous solutions of the acid. The secondary ionization is so small (see below) that it scarcely contributes to the conductivity of carbonic acid and consequently it can be neglected in the determination. The value found for the first ionization constant is:

$$K'_{\text{Ionisation}} = 3.04 \times 10^{-7} \tag{21}$$

The second ionization constant of carbonic acid (equation IV) was calculated by Bodlaender from Shields's experiments on the hydrolysis of sodium carbonate, but, owing to an error in Shields's calculations, found by McCoy, the value given by Bodlaender (1.295×10<sup>-11</sup>) can not be accepted. It was recalculated by McCoy from Shields's results and found to be  $12.0 \times$ 10-11 or ten times as large as Bodlaender's value. McCoy then determined the constant by a study of the condition of equilibrium between sodium bicarbonate, carbonate, and carbonic acid, and from the values for decinormal solutions of bicarbonate he obtained  $6.0 \times 10^{-11}$ , which was only half as large as the constant calculated from Shields's data; 0.3 normal and normal bicarbonate solutions gave still other values.

A recalculation of this constant, which is important for our work, was made from McCoy's data, and corrections which were indicated by the latter, but not carried out, were made for changes in the solubility of carbon

<sup>&</sup>lt;sup>1</sup> Liebig's Annalen, 93, 20 (1855); Dammer, Handbuch der Anorganischen Chemie II, 372. See also Geffcken, Zeitschrift für Physikalische Chemie, 49, 257 (1904). <sup>2</sup> Dammer, Handbuch der Anorganischen Chemie, II, 1, 367.

Journal of the Chemical Society, London, 77, 8 (1900). Loc. cit.

Zeitschrift für Physikalische Chemie, 12, 174 (1893).

<sup>&</sup>lt;sup>1</sup> Loc. cit.

<sup>16</sup> 

dioxide in salt solutions and for the changes in the ionisation of salts in mixtures. While the recalculation did not change the order of the results, it removed the uncertainty as to the effect of these corrections.

From the two equations for the ionization of carbonic acid, III and IV, we get by dividing III by IV:

$$\frac{C_{HCO_{3}}^{2}}{C_{CO_{3}} \times C_{H_{2}CO_{3}}} = \frac{K'_{Ionisation}}{K''_{Ionisation}} = K$$
 (22)

The constant K can be readily calculated from any of McCoy's results, and then

$$K''_{Ionisation} = \frac{K'_{Ionisation}}{K} = \frac{3.04 \times 10^{-7}}{K}$$
 (23)

In 0.0999 normal solution of sodium bicarbonate according to table 2,1 under a partial pressure of 0.00161 atmosphere (P), McCoy found 68.2 per cent bicarbonate and 31.8 per cent carbonate. The degrees of ionization of these salts can be put equal to those of sodium acetate and sodium sulphate, respectively, similar salts ionizing very much alike, and the determinations of the ionization of the acetate and sulphate from their conductivities being far more reliable than the estimations from the conductivities of bicarbonate and carbonate solutions which really represent complex mixtures. A consideration of the curves for the conductivities for sodium carbonate and sulphate shows them in fact to be practically parallel for more concentrated solutions in which the hydrolysis of the carbonate is small, but for more dilute hydrolyzed solutions the curve for the carbonate bends and cuts the sulphate curve, which is an indication of hydrolysis. Hence it was deemed safer to determine the degree of ionization from the sulphate and acetate curves. Then in the experiment mentioned we have

$$C_{HCO_2} = 0.0999 \times 0.682 \times 0.783 = 0.05335$$
  
 $C_{CO_2} = 0.0999 \times 0.5 \times 0.318 \times 0.687 = 0.01091$ 

The solubility of carbon dioxide in salt solutions is smaller than in water. A correction was made for this by putting the solubility equal to that of 0.1 normal potassium chloride solution. From the results of Geffcken, whose work is the best on the subject, the decrease in the coefficient of absorption is practically proportionate to the concentration of the salt, the coefficients for pure water, for 0.5 molar and 1.0 molar solutions of potassium chloride forming practically a rectilinear curve, the concentra-tions and the coefficients being used as coördinates. By interpolation on the curve, the coefficient of absorption for 0.1 molar potassium chloride at 25°, the temperature at which McCoy worked, is 0.742, reduced to

<sup>&</sup>lt;sup>1</sup> Loc. cit.
<sup>2</sup> The degree of ionization of 0.1 molar sodium acetate, Kohlrausch und Holborn, Leitfähigkeiten, pp. 159 and 200, is calculated as 0.783.

The degree of ionization of 0.1 equivalent sodium sulphate, ibid., is 0.687. In a mixture of the two, the degrees of ionization would be very slightly modified, but a calculation of the change made on the basis of the principle of isohydric solutions showed the correction to be negligible.

<sup>3</sup> Loc. cit.

0°.760 mm, and

$$k_{\rm gas} = \frac{0.742}{22.4} = 0.03313*$$

Then

$$C_{H_6CO_3} = 0.03313 \times 0.00161 = 5.33 \times 10^{-6}$$

Inserting the values determined for the functions in equation (22) we have

$$\frac{\mathrm{C^2_{HCO_2}}}{\mathrm{C_{H_2CO_2}}\!\times\!\mathrm{C_{CO_3}}}\!=\!\frac{0.05335^{3}}{0.01991\!\times\!5.33\!\times\!10^{-5}}\!=\!4,895\!=\!\mathrm{K}$$

The second ionization constant of carbonic acid is, then, according to equation (23)

 $K''_{H_2CO_2} = \frac{3.04 \times 10^{-7}}{4895} = 6.21 \times 10^{-11}$ 

A similar calculation for experiment 6, which McCoy considered as presenting the most favorable conditions for accuracy and in which the partial pressure of carbon dioxide was 0.00404 atmosphere, gave  $6.205 \times 10^{-11}$ .

For experiment 1, table 3,† 0.3 normal bicarbonate was used, 57.9 per cent remaining as bicarbonate, 42.1 per cent being converted into carbonate when equilibrium was established under a partial pressure of carbon dioxide of 0.00319 atmosphere. We have ‡ as before

$$C_{HCO_2} = 0.3 \times 0.579 \times 0.70 = 0.1216$$
  
 $C_{CO_2} = 0.3 \times 0.5 \times 0.421 \times 0.584 = 0.0369$ 

By interpolation of Geffcken's results, the coefficient of absorption of carbon dioxide by 0.3 normal potassium chloride at 25° is 0.720 and  $k_{\rm gas}$  is 0.03214.§ Hence

$$C_{H_4CO_2} = 0.03214 \times 0.00319 = 1.02 \times 10^{-4}$$

and

$$\frac{C_{^{2}HCO_{a}}}{C_{H_{a}CO_{a}} \times C_{CO_{a}}} = \frac{0.1216^{2}}{1.02 \times 10^{-4} \times 0.0369} = 3,910 = K$$

According to equation (23) we have, then,

$$K''_{Ionisation} = 7.8 \times 10^{-11}$$

We will use the mean of the two constants or 7×10<sup>-11</sup> for the calculations made in this investigation.

#### THE DETERMINATION OF THE SOLUBILITY CONSTANT FOR CALCIUM CARBONATE.

With the aid of the constant for the secondary ionization of carbonic acid, of the constant for its primary ionization as determined by Walker and Cornack, and the experiments of Schloesing on the solubility of calcium carbonate under the influence of varying partial pressures of carbon dioxide,

<sup>\*</sup> McCoy used 0.0338 without correction for the changed solubility.
† Page 456, loc. cit.
‡ The degree of ionisation of 0.3 normal sodium acetate, loc. cit., is 0.70; of 0.3 equivalent sodium sulphate, loc. cit., it is 0.584.
§ 0.0338 for pure water.

we can now determine the value for the solubility product of calcium carbonate  $^a$   $C_{Ca} \times C_{CO_s} = K_{CaCO_s}$ 

to which the precipitation of calcium carbonate is subject. As explained above, the solution may be considered just saturated whenever the product of the ion concentrations is equal to this constant. Excess of carbonic acid increases the solubility through its hydrogen ions, which form bicarbonate ions  $HCO_3$  with the carbonate ions  $CO_2$  of the calcium carbonate. Since  $C_{Ca} \times (C_{CO_3} - x) < K_{CaCO_3}$ 

the solution is no longer saturated with calcium carbonate and the solid carbonate will go into solution until we again have:

$$C'_{Ca} \times C'_{COa} = K_{CaCOa}$$

the concentrations  $C'_{Co}$  and  $C'_{CO}$ , being unequal now, calcium ions being in excess.

As stated on page 242, the solubility will depend on all four of our fundamental equations I to IV (on p. 242), the functions being dependent on the various constants. They may all be combined as follows: Dividing equation III by IV, we have first:

$$\frac{\mathrm{C^{2}_{HCO_{3}}}}{\mathrm{C}_{\mathrm{CO_{3}}} \times \mathrm{C}_{\mathrm{H_{2}OO_{3}}}} = \frac{\mathrm{K'_{Ionisation}}}{\mathrm{K''_{Ionisation}}} \tag{24}$$

We may substitute in this equation for  $C_{CO_2}$  its value as obtained from equation I, viz.  $\frac{K_{CaCO_2}}{C_{Ca}}$ , and have

$$\frac{C_{Ca}\!\times\!C^{2}_{HCO_{2}}}{K_{CaCO_{3}}\!\times\!C_{H_{5}CO_{2}}}\!=\!\frac{K'_{Ionisation}}{K''_{Ionisation}}$$

or

$$\frac{C_{Ca} \times C^{2}_{HCO_{2}}}{C_{H_{2}CO_{2}}} = K_{CaCO_{2}} \times \frac{K'_{Ionisation}}{K''_{Ionisation}}$$
(25)

Now, when calcium carbonate is dissolved under the influence of excess of carbonic acid in the absence of any other calcium salts, as was the case in Schloesing's experiments, practically all of the calcium is present as bicarbonate, the quantity of carbonate being minimal and quantitatively negligible in comparison with the bicarbonate. Since

$$Ca(HCO_3)_2 = Ca'' + 2HCO_3'$$
 (26)

the concentration of the calcium ions will be half that of the bicarbonate ions  $C_{Ca} = \frac{1}{2}C_{HCO_3}$  (27)

and by substituting this value in (25) we have

$$\frac{C_{\text{H}_2\text{CO}_3}^3}{C_{\text{H}_2\text{CO}_3}} = 2K_{\text{CaCO}_3} \times \frac{K'_{\text{Ionization}}}{K''_{\text{Ionization}}}$$
(28)

For the concentration of the dissolved carbonic acid we have, according to II:  $C_{H_2CO_3} = k_{gas} \times P$ (29)

a Vide Bodlaender, loc. cit.

where  $k_{gas}$  is expressed in molar terms and P is the partial pressure of the carbon dioxide above the solution (see p. 243).

Equation (28) may be transformed then into

$$\frac{\mathrm{C^{9}_{HCO_{2}}}}{P} = 2 \times k_{\mathrm{gas}} \times \frac{\mathrm{K'}_{\mathrm{Ionisation}}}{\mathrm{K''}_{\mathrm{Ionisation}}} \times \mathrm{K}_{\mathrm{CaCO_{2}}}$$
(30)

an equation which holds for saturated solutions of calcium carbonate and bicarbonate in equilibrium with solid calcium carbonate and gaseous carbon dioxide of any pressure P at a given temperature. The composition of such saturated solutions has been determined by Schloesing, and since from his data the values of CHCO, and of P can be ascertained, and since all the constants excepting the solubility product K<sub>CaCO<sub>2</sub></sub> are now known, the value of this constant can now be determined.a

The value of the first ionization constant of carbonic acid is  $3.04 \times 10^{-7}$ ; the value of the second ionization constant is 7×10<sup>-11</sup>. Geffcken's a recent very exact determinations of the absorption of carbon dioxide by water, made with an improved apparatus, give somewhat higher values than found by Bunsen years ago. At 16°, the temperature at which Schloesing's determinations were made, by interpolation of the values found by Geffcken for 15° and 25°, the coefficient of absorption is found to be 0.9890 (reduced to 0°.760 mm.) instead of 0.9753. The change in solubility produced by the presence of the small amount of salts present (in Schloesing's experiments this is only 0.01 equivalent, as an average) is negligible. The coefficient

0.9890 corresponds to a constant  $k_{gas}$  equal to 0.04415 in molar terms. Substituting the values of our three known constants in equation (30)

we obtain:

$$\frac{\text{C°}_{\text{HCO}_2}}{P} = 2 \times 0.04415 \times \frac{3.04 \times 10^{-7}}{7 \times 10^{-11}} \times \text{K}_{\text{CaCO}_2}$$
$$= 383.4 \times \text{K}_{\text{CaCO}_2}$$

and

$$\sqrt[3]{K_{\text{CaCO}_2}} = \frac{C_{\text{HCO}_2}}{7.264 \times \sqrt[3]{P}}$$
 (31)

Schloesing's results give the total amount of calcium carbonate dissolved: it is present almost exclusively as calcium bicarbonate. The degrees of ionization, a, of the calcium bicarbonate in the various solutions may be put equal to the degrees of ionization of calcium acetate in equivalent concentrations; then, in any given solution

$$C_{HCO_2} = \alpha \times \frac{1}{2} C_{Ca(HCO_2)_2}$$
 (32)

<sup>&</sup>lt;sup>a</sup> Bodlaender, loc. cit. <sup>b</sup> Page 243. <sup>c</sup> Page 245.

d Loc. cit.

<sup>\*</sup>Bodlaender used calcium chloride and nitrate for this purpose. As salts of organic acids usually are somewhat less ionized than salts of stronger inorganic acids, it seemed better to ascertain the degree of ionization by comparison with calcium acetate. The conductivities for calcium acetate are given in Kohlrausch and Holborn's Leitfähigkeiten on page 161 and the degrees of ionization are calculated in the usual way. There is an average difference of about 4 per cent between these coefficients of ionization and those used by Bodlaender.

In table 4 the data are tabulated and the calculated values for  $\sqrt[4]{K_{CaCO_2}}$  given. Column 1 gives P the pressure of carbon dioxide in atmospheres, column 2 the solubility of calcium carbonate as determined by Schloesing and expressed in gram equivalents of calcium bicarbonate  $\left(\frac{\text{Ca}(\text{HCO}_3)_2}{2}\right)$  per liter. Column 3 gives the degree of ionization a of the corresponding calcium acetate solutions, column 4 the concentration of acid carbonate ions,  $C_{\text{HCO}_3}$ , as calculated from the numbers given in columns 2 and 3. In the last column we have the values for  $\sqrt[4]{K_{\text{CaCO}_2}}$  as calculated according to equation (31).

T.	<b>DT</b> 1	- 4	ı
LA	BЫ		Ł.

CO3	Atm. ( <i>P</i> )	½ Ca(HCO₂)₂	100a	CHCO3	10 <sup>6</sup> × <sup>3</sup> /K <sub>CaCO<sub>8</sub></sub>
1 2 3 4 5 6 7 8 9 10 11	0.000504 .000808 .00333 .01387 .02820 .05008 .1422 .2538 .4167 .5533 .7297 .9841	0.001492 .001700 .002744 .004462 .005930 .007200 .01068 .01327 .01575 .01771 .01944 .02172	90.9 90.2 88.8 87.1 85.9 85.0 82.8 81.0 79.8 79.1 78.4	0.001356 .001533 .002437 .003886 .005097 .006120 .008828 .01074 .01257 .01402 .01525 .01684	235 227 225 225 231 229 233 234 232 233 233

The mean value for  $\sqrt[3]{\text{KCaCO}_2}$  is 0.002325.

The agreement among the values found for  $\sqrt[4]{K_{CaCO_2}}$  under a partial pressure of carbon dioxide ranging from  $\frac{1}{2000}$  atmosphere to 1 atmosphere is excellent, and this agreement forms a very good test of the correctness of the whole theoretical treatment, such a constant resulting from a consideration of the conditions of equilibrium on the basis of the theory of ionization.<sup>1</sup>

From the value for  $\sqrt[4]{K_{CaCO_3}} = 0.002325$ , we find the solubility product itself  $C_{Ca} \times C_{CO_3} = K_{CaCO_3} = 1.26 \times 10^{-8}$ (33)

It may be pointed out that this method of determining the solubility product constant of calcium carbonate must be far more reliable than a deter-

¹As Bodlaender (loc. cit.) points out, it is clear from the theoretical treatment that the same equation applies to the effect of carbon dioxide on the solubility of other difficultly soluble salts, such as barium carbonate, the only difference being that the solubility product constant of barium carbonate ( $C_{Ba} \times C_{CO_3} = K_{BaCO_3}$ ) is substituted for the constant for calcium carbonate. All the other expressions remain the same. Bodlaender has used the results of Schloesing on the solubility of barium carbonate as affected by carbon dioxide to calculate in the same way the value for  $\sqrt[3]{K_{BaCO_3}}$  and obtained again an excellent agreement among the values for the constant. Only the numerical value of the constant, not the constancy of the results, is affected by the corrections made in this paper, namely, in the value of the second ionization constant for carbonic acid and in the method of calculation of the degrees of ionization a. As the value for  $\sqrt[3]{K_{BaCO_3}}$  is not of interest in this investigation, the data were not recalculated.

mination based on the direct solubility of calcium carbonate in water. The latter method gives excellent results with salts like silver chloride, calcium or barium sulphate, but calcium carbonate is largely hydrolyzed by water into the hydroxide and carbonic acid and bicarbonate, and this hydrolysis, together with the possibility of absorption of carbon dioxide and consequent change in the equilibrium conditions, affects these direct determinations. Bodlaender has estimated that about 80 per cent of the calcium carbonate is decomposed by water in its saturated solution in pure water. In Schloesing's experiments the hydrolysis is practically completely overcome by the measurements being made in the presence of an excess of carbon dioxide. No calculations were made by Bodlaender as to the extent of any hydrolysis in these experiments of Schloesing, but we can readily determine it as follows: In experiment 1, in which we have the smallest pressure of carbon dioxide and therefore the most favorable conditions for hydrolysis, we have as the pressure of carbon dioxide (P) 0.000504 atmosphere. Consequently, according to equation (29)

$$C_{H_8CO_8} = 0.04415 \times 0.000504 = 2.225 \times 10^{-4}$$

According to the table we have

$$C_{HCO_a} = 0.001356$$

Now, for carbonic acid we have (equation III, p. 242),

$$C_{\rm H} \times C_{\rm HCO_a} = 3.04 \times 10^{-7} \times C_{\rm H_sCO_a}$$

and inserting the given values for CHCO, and CH,CO, we find:

$$C_{\rm H} = \frac{3.04 \times 10^{-7} \times 2.225 \times 10^{-4}}{0.001356} = 4.99 \times 10^{-4}$$

Now, for the ionisation of water at 16°, we have:

$$C_H \times C_{OH} = 0.55 \times 10^{-14}$$

and consequently

$$C_{OH} = \frac{0.55 \times 10^{-14}}{4.99 \times 10^{-4}} = 1.1 \times 10^{-4}$$

Calcium bicarbonate, the chief salt in solution, is hydrolyzed according to  $\frac{1}{2}Ca(HCO_2)_2 + HOH = \frac{1}{2}Ca(OH)_2 + H_2CO_2$ 

and since the equivalent concentration of the bicarbonate ions in experiment 1 is 0.001356, the part hydrolyzed is  $1.1 \times 10^{-4}/0.001356$ , or about 0.08 per cent. So, even in this first, least favorable experiment, the hydrolysis is negligible. In experiment 5, we find in a similar way

$$C_{\rm H} = 7.43 \times 10^{-8}$$
  $C_{\rm OH} = 7.40 \times 10^{-8}$ 

and the part hydrolyzed is  $7.4 \times 10^{-6}/0.0051$ , or 0.0014 per cent.

Hydrolysis is reduced therefore to almost nothing, and the value found for  $K_{CaCO_2}$ ,  $1.26 \times 10^{-8}$ , needs no correction from this source.

## EQUILIBRIUM BETWEEN CALCIUM CARBONATE AND GYPSUM.

THE SOLUBILITY PRODUCT OF CALCIUM SULPHATE.

For a saturated solution of gypsum, ionized according to

$$CaSO_4 = Ca'' + SO_4'' \tag{34}$$

we may put, as we did for calcium carbonate,

$$C_{Ca} \times C_{SO_4} = K_{CaSO_4} \tag{35}$$

The value of this solubility product constant can be determined from the solubility of calcium sulphate in water and its degree of ionization in the saturated solution, since the salt dissolves without any hydrolytic decomposition. Kohlrausch and Rose' give the solubility of gypsum at 18° as 2.07 g. (anhydrous calcium sulphate) per liter of water. This represents a concentration of 2.07/136.1 or 0.0152 gram molecule and 0.0304 gram equivalent of calcium sulphate. The degree of ionization is best ascertained from its conductivity in the saturated solution; the specific conductivity of the solution is given 2 as 0.001891 reciprocal ohms at 18°; its equivalent conductivity is, then

$$A_{\text{CaSO}_4} = \frac{0.001891 \times 1,000}{0.0304} = 62.2$$

The conductivity of calcium sulphate at extreme dilution<sup>2</sup> is 123 and its degree of ionization in the saturated solution therefore 62.2/123 or 50.6 per cent. Then  $C_{Ca} = C_{SO_4} = 0.0152 \times 0.506 = 0.00769$ and

$$K_{CaSO_4} = C_{Ca} \times C_{SO_4} = 0.00769^2 = 5.92 \times 10^{-4}$$
 (36)

The solubility product of calcium sulphate at 18° is therefore  $5.92 \times 10^{-4}$ .

#### CALCIUM SULPHATE AND CALCIUM CARBONATE.

If we have a solution saturated both with calcium sulphate and with calcium carbonate, for instance in contact with both solid salts, we have in the saturated solution simultaneously

$$C_{Ca} \times C_{CO_a} = K_{CaCO_a} \tag{37}$$

and

$$C_{Ca} \times C_{SO_4} = K_{CaSO_4} \tag{38}$$

The value for C<sub>Ca</sub> is the same now in both equations, representing as it does the total concentration of calcium ions, irrespective of their source from sulphate, carbonate, or bicarbonate. Then, dividing equation (38) by equation (37), we have for a solution in equilibrium with both salts at 16° to 18°

$$\frac{C_{SO_4}}{C_{CO_3}} = \frac{K_{CaSO_4}}{K_{CaCO_8}} = \frac{5.92 \times 10^{-6}}{1.26 \times 10^{-6}} = 4,700$$
 (39)

<sup>&</sup>lt;sup>1</sup> Zeitschrift für Physikalische Chemie, 12, 241 (1893).

<sup>2</sup> Kohlrausch and Holborn, loc. cit., p. 77.

<sup>3</sup> Ibid., p. 200, table 8b.

<sup>4</sup> The value for K<sub>CaCO2</sub> determined at 16° is used; no correction is made for the difference of 2°.

This means that the concentration of sulphate ions must be about 5,000 times as large as that of the carbonate ions in a solution saturated with both salts, and consequently one or the other salt will come down first pure, when precipitation from a mixture is effected, until this ratio is reached. Under ordinary conditions obtaining in nature or in laboratory experiments, the excess of sulphate ions is not as large as this, and so the carbonate is precipitated first until the concentration of carbonate ions has fallen to about one five-thousandth that of the sulphate ions. On the other hand, if in such a solution, which is in equilibrium with both solid salts, the concentration of the sulphate ions is by any means increased, e.g., by addition of some sodium or potassium sulphate, the solution will be oversaturated with calcium sulphate  $[C_{C_0} \times C'_{SO_4} > K_{C_0SO_4}]$ , gypsum will be precipitated, and owing to the loss of calcium ions the solution will now be undersaturated in regard to the carbonate  $[(C_{Ca}-x)\times C_{CO_s}< K_{CaCO_s}]$ , and solid calcium carbonate must dissolve until the above ratio is reached. In the same way the order of precipitation may be reversed if by any means the concentration of the carbonate ions in a solution is persistently kept below one five-thousandth that of the sulphate ions during the process of precipitation or crystallization, for instance, by the addition of an acid.1

For an aqueous solution saturated with gypsum and calcium carbonate at about 18°, the concentration of calcium ions may be taken as 0.00769, as practically all of the calcium ions are derived from the sulphate. The concentration of carbonate ions in such a solution is, then,

$$C_{\text{CO}_8} = \frac{K_{\text{CaCO}_8}}{C_{\text{Ca}}} = \frac{1.26 \times 10^{-8}}{0.00769} = 1.64 \times 10^{-8}$$
 (40)

With the aid of this value we can calculate, for varying partial pressures of carbon dioxide, the maximum proportions of calcium carbonate and bicarbonate which can be present in solutions saturated with gypsum and calcium carbonate at approximately 18°.

CALCIUM SULPHATE, CARBONATE, AND BICARBONATE, WITH REFERENCE TO GIVEN PARTIAL PRESSURES OF CARBON DIOXIDE.

The present average partial pressure of carbon dioxide in the atmosphere is 0.0003 atmosphere. We may ask what is the maximum amount of calcium present as carbonate and bicarbonate in 1 liter of a solution which is in equilibrium with this partial pressure of carbon dioxide and which is saturated both with gypsum and with calcium carbonate. The significance of this quantity will be discussed presently; it can be calculated as follows, with the aid of the equations developed above. We have:

$$\begin{array}{l} C_{\rm H} \times C_{\rm HCO_2} = K'_{\rm Ionisation} \times C_{\rm H_2CO_2} & {\rm (III)} \\ C_{\rm H} \times C_{\rm CO_2} = K''_{\rm Ionisation} \times C_{\rm HCO_2} & {\rm (IV)} \end{array}$$

$$C_{\text{TZ}} = k_{\text{max}} \times C_{\text{CO}} \tag{II}$$

<sup>(</sup>II) $C_{H_1CO_2} = k_{gas} \times C_{CO_2}$ 

<sup>&</sup>lt;sup>1</sup> Analogous relations have been developed experimentally and theoretically in connection with Guldberg and Waage's classical work on barium sulphate and carbonate. *Vids* Nernst, Theoretical Chemistry, p. 533 (1904), and Findlay, Zeitschrift für Physikalische Chemie, 34, 409 (1900).

Combining the three equations by dividing III by IV and multiplying by II, we find:

$$C_{HCO_2}^2 = \frac{K'_{Ionisation}}{K''_{Ionisation}} \times k_{gas} \times C_{CO_2} \times C_{CO_3}$$
(41)

and

$$C_{HCO_2} = \sqrt{\frac{K'_{Ionisation}}{K''_{Ionisation}}} \times k_{gas} \times C_{CO_2} \times C_{CO_2}$$
(42)

Now, for a solution saturated with calcium carbonate and gypsum at about 18°, Coo, may be said as a first approximation to have a maximum value of  $1.64 \times 10^{-4}$  as shown above (equation 40), the calcium ions produced from the bicarbonate being neglected in this first approximation and only those from the gypsum being considered. At 18° the solubility constant for carbon dioxide,  $k_{\rm gas}$ , is 0.04183 if  $C_{\rm CO_{\rm s}}$  be expressed in atmospheres. In the given case  $C_{\rm CO_{\rm s}}$  is 0.0003 atmosphere. Inserting all these values and the two known ionization constants of carbonic acid into equation (42), we find

$$C_{HCO_3} = \sqrt{\frac{3.04 \times 10^{-7}}{7.0 \times 10^{-11}}} \times 0.04183 \times 0.0003 \times 1.64 \times 10^{-6}$$

and

$$C_{HCO_2} = 0.0003$$

For the calcium ions belonging to the bicarbonate we have

$$C_{Ca} = \frac{1}{2}C_{HCO_a} = 0.00015$$

We have found then the ionized portion of the calcium bicarbonate in the saturated solution. To determine the total dissolved bicarbonate its degree of ionization in the mixture must be ascertained. Its degree of ionization will depend not on its own concentration alone, but, according to the principle of isohydric solutions, also on that of the calcium sulphate present. We may imagine, according to the method of Arrhenius, the water divided between the two salts in such a way that each in its portion yields the same concentration of the common ion calcium. Since there is 50 times as much sulphate as bicarbonate, the latter will secure only about 2 per cent of the water, the sulphate about 98 per cent, and the sulphate will ionize practically as if it were present alone. Its degree of ionization is then 50.6 per cent (p. 250), and its concentration of calcium ions 0.00769 or 0.01538 calcium ion equivalent. This, then, must also be the concentration of the calcium ion equivalents in the isohydric bicarbonate solution, and so we have  $C_1Ca(HCO_2)_2 \times \alpha = 0.01538$ 

¹ The amount of calcium bicarbonate found in solution by this first approximation corresponds to 0.00015 gram ion of calcium. The calcium ions from the carbonate are negligible and therefore the total concentration of calcium ions from sulphate and bicarbonate is 0.00769+0.00015 or 0.00784, and the maximum value for CCO₂ is, corrected, 1.26×10<sup>-8</sup>/0.00784 (equation 40) or 1.16×10<sup>-8</sup> in place of 1.64×10<sup>-8</sup>. No correction was made for this small difference, the results of the first approximation being considered sufficiently accurate, especially in view of the facts that the solubility of calcium sulphate will be slightly affected by the presence of the bicarbonate in such a way as to counterbalance this error and that the degrees of ionization of salts are uncertain.

² Geffcken, loc. cit. The total salt concentration (0.03 mole) is too small to require a correction for the changed solubility of carbonic acid.

By considering the bicarbonate to ionize like the acetate, we easily find by trial that ½Ca(HCO<sub>2</sub>)<sub>2</sub> has a concentration of 0.0196 equivalent, whose degree of ionization is found from the conductivity curve for calcium acetate to be 78.5 per cent

$$0.0196 \times 0.785 = 0.01538$$
 calcium ion equivalent,

as required by the isohydric principle.1

Thus we find the degree of ionization of the calcium bicarbonate to be 78.5 per cent. The ionized portion of the bicarbonate is 0.00015 gram molecule per liter, as was found above; consequently the total amount of calcium bicarbonate in 1 liter is 0.00015/0.785 or 0.00019 gram molecule.

A solution saturated with gypsum and calcium bicarbonate and carbonate at about  $18^{\circ}$  under a partial pressure of 0.0003 atmosphere would contain therefore  $1.9 \times 10^{-4}$  gram molecule of calcium bicarbonate. Such a solution by evaporation would deposit an equivalent amount of calcium carbonate, or 0.019 gram of calcium carbonate per liter,<sup>2</sup> and gypsum deposited by evaporation from such a solution would be contaminated with 0.019/2.07 or 0.9 per cent of calcium carbonate (referred to the anhydrous gypsum).<sup>2</sup>

For a solution saturated at 18° with gypsum and with calcium carbonate and bicarbonate under a partial pressure of carbon dioxide 10 times as great as the present average value in the atmosphere, the proportion of calcium bicarbonate in solution can be calculated in a similar fashion. As a first approximation we have

$$\begin{split} C_{\text{HOO}_2} &= \sqrt{\frac{3.04 \times 10^{-7}}{7 \times 10^{-11}}} \times 0.04183 \times 0.003 \times 1.64 \times 10^{-8} \\ &= \sqrt{10} \times 0.0003 = 0.00095 \end{split}$$

Since  $C_{Ca}$  is  $\frac{1}{2}C_{HCO}$ , the concentration of calcium ions in solution would be close to 0.00769 + 0.00047 or 0.00816, and consequently in the saturated solution the maximum value for the carbonate ions is

$$C_{CO_4} = \frac{1.26 \times 10^{-6}}{0.00816} = 1.54 \times 10^{-6}$$

Introducing this corrected value into the above equation, we find

$$C_{HCO_2} = 0.00916$$
 and  $C_{Ca} = 0.00046$ 

The degree of ionization for the calcium bicarbonate is found by the method used above to be 78 per cent and the total calcium bicarbonate, ionized and non-ionized, in 1 liter, is 0.000458/0.78 or 0.00059 gram molecule.

A solution saturated with gypsum and calcium carbonate and bicarbonate at 18° under a partial pressure of 0.003 atmosphere would contain therefore  $5.9 \times 10^{-4}$  gram molecules of calcium bicarbonate per liter, and by

 $<sup>^1</sup>$  20 c.c. of a 0.0196 equivalent or 0.0098 molar solution of calcium bicarbonate would contain 0.000196 gram molecule and 0.000196 $\times$ 0.785=0.00015 C<sub>Ca</sub>, the total concentration of calcium ions derived from the bicarbonate in solution. The bicarbonate ionizes as if it were all dissolved in about 20 c.c. water

it were all dissolved in about 20 c.c. water.

The amount of calcium carbonate in solution in 1 liter is so minute as to be negligible.

Cf. Findlay, loc. cit.

evaporation such a liter would deposit 0.059 gram of calcium carbonate as a contamination of the gypsum or 0.059/2.07, or 2.85 per cent (referred to the dehydrated gypsum). Briefly the amount of calcium carbonate produced under a tenfold increase in the partial pressure for carbon dioxide is very closely proportionate to the square root of 10.

For a solution saturated at 18° with gypsum, calcium carbonate and bicarbonate under a partial pressure one-tenth as great as its present average value, viz, 0.00003 atmosphere, we may put

$$C_{HCO_2} = \sqrt{0.1} \times 0.0003 = 0.000095$$

and C<sub>Ca</sub> 0.0000475. The degree of ionization is 78.5 per cent, and the total dissolved bicarbonate is 0.0000475/0.785 or 0.00006 gram molecule per liter.

A solution saturated with gypsum, calcium carbonate and bicarbonate at 18° under a pressure of 0.00003 atmosphere of carbon dioxide would contain  $6 \times 10^{-6}$  gram molecules of calcium bicarbonate per liter, and would deposit by its evaporation 0.006 gram of calcium carbonate, producing a contamination of 0.006/2.07 or 0.3 per cent (referred to dehydrated gypsum).

In table 5 the results are summarized for the calculations made for aqueous solutions under the conditions named. Column 1 gives the carbon dioxide pressure in atmospheres; column 2 gives weight in grams of calcium sulphate present in one liter; column 3 shows similarly the calcium bicarbonate present, but expressed in grams of carbonate per liter. Columns 4 and 5 give the values of columns 2 and 3 in terms of gram molecules per The last column gives the proportion of calcium carbonate which would be found in gypsum separating from such an ideal solution by evaporation, the proportion referring to dehydrated gypsum.1

CaSO<sub>4</sub> (grams). CaCO<sub>3</sub> (grams). CO<sub>2</sub> (atmosp.). CaSO<sub>4</sub> (moles). CaCO<sub>3</sub> (moles). Per cent CaCO<sub>2</sub>. 0.00003 2.07 2.07 0.00006 .00019 0.006 0.0152 0.30

.0152

0152

0.90

2.85

.00059

TABLE 5.

#### DISCUSSION.

.019

.0003

2.07

003

The significance of these results is as follows: For an ideal condition, if the natural waters of the earth were supposed to contain only lime salts, that is the sulphate, carbonate and bicarbonate in equilibrium with the carbon dioxide of the atmosphere, then by evaporation they would deposit first, as is now the case, until the solution became saturated with gypsum, all the calcium carbonate in solution in excess of the amounts given in

¹ Cameron and Seidell, Journal of Physical Chemistry, 5,652 (1901), got experimentally 0.037 g. calcium carbonate or 1.9 per cent from a solution containing 1.93 grams calcium sulphate (0.0143 mole) in equilibrium with air. The partial pressure of the carbon dioxide in the air is not specified (laboratory air is notably richer in carbon dioxide) and no temperature is mentioned, but it probably was between 22° and 25° (see pp. 643 and 650). Only one determination is reported, and under the circumstances we must be content with the fact that the result is of the order calculated. (Vide McCoy, American Chemical Journal, 29, 461 (1903), who also questions the quality of the air used by Cameron.)

table 5, in columns 3 and 5, depending on the partial pressure of the atmospheric carbon dioxide. When the solution becomes saturated with gypsum this will, by continued evaporation, crystallize out, but no matter whether it is deposited in the same locality as, or in some other locality than, the first great deposit of calcium carbonate, the gypsum must inevitably be continuously contaminated with some calcium carbonate, varying from 0.3 to 2.85 per cent, according to the partial pressure of the carbon dioxide in the atmosphere within the limits given. Perfectly pure gypsum would not be formed under such conditions. Vice versa, a very exact determination of the amount of calcium carbonate present in gypsum prepared under such ideal conditions could be used as a criterion of the carbon dioxide content of the atmosphere under which the gypsum was formed.

Obviously such a hypothetical ideal condition as to constancy of temperature and purity of the solutions never existed on the earth, and the presence of other salts, notably of sulphates even in smaller quantities and of chlorides in larger amounts, modifies decidedly the numerical values determined above: the foundation for the study of the relations of gypsum and calcium carbonate having been laid for this ideal condition, it seemed desirable to pursue the inquiry to ascertain, at least roughly, the influence the presence of other salts would have, especially the sulphates of magnesium, potassium, and sodium, and the chloride of sodium. In the following pages an attempt has been made to estimate only roughly the influence of the presence of other sulphates.

# CALCIUM SULPHATE, CARBONATE, AND BICARBONATE IN THE PRESENCE OF SULPHATES.

The solubility of a difficultly soluble salt like calcium sulphate depending on its solubility product

 $C_{Ca} \times C_{SO_4} = K_{CaSO_4}$ 

the presence of other sulphates in solutions that are not too concentrated to interfere with the application of the laws of solution would, through the increase in the concentration of the sulphate ions, have as its chief effect a decrease in the concentration of the calcium ions, according to the equation just given. Since about half of the gypsum is ionized in its saturated solution, a decrease in the concentration of its calcium ions would imply a decrease in the solubility of gypsum. The decreased solubility of the gypsum or the decrease in the concentration of calcium ions would, vice versa, increase the solubility of calcium carbonate and bicarbonate; so, from both causes, gypsum crystallizing from a not too concentrated sulphate solution under the conditions we are studying might be expected to be more contaminated with calcium carbonate than was found for aqueous solutions.

In order to study these effects, it was decided to examine from this point of view the probable effect of the sulphates of magnesium, potassium, and sodium in the proportion in which they are found with calcium sulphate in the present sea-water, determining also the effect of varying partial pressures of atmospheric carbon dioxide, as was done before.

<sup>&</sup>lt;sup>1</sup> Such a change of locality was suggested to the author by Dr. O. Willcox.

At present we have in sea-water in 1,000 parts 1.239 grams or 0.009 gram molecule of calcium sulphate, 1.617 grams or 0.0135 gram molecule of magnesium sulphate, and 0.860 gram or 0.005 gram molecule of potassium sulphate.1 Such a solution would contain 0.0275 mole or 0.055 gram equivalent of total sulphates. The degrees of ionization of calcium and magnesium sulphates are practically the same, and while potassium sulphate ionizes far more readily, it forms a relatively small component of the system, and we can, with sufficient accuracy for our purpose, consider the degree of ionization for the sulphates to be that of a 0.05 equivalent magnesium sulphate solution or 48 per cent. Then

$$C_{804} = 0.0275 \times 0.48 = 0.0132$$
  
 $C_{0a} = 0.0091 \times 0.48 = 0.0044$ 

and

$$C_{C_0} \times C_{SO_4} = 0.000058$$

Since for a saturated solution the solubility product constant is 0.000059 (K<sub>CaSO<sub>4</sub></sub>), we see that this sea-water would be almost saturated with gypsum were it not for the modifying influence of the presence of a large proportion of sodium chloride and other salts in it.4

A purely aqueous solution of the above composition should be nearly saturated with gypsum and a large part of the latter should crystallize out during its concentration say to one-quarter its original volume. If at the beginning, when the solution is practically saturated with gypsum, it also at the same time be considered to be saturated with calcium carbonate and bicarbonate in equilibrium with a partial pressure of 0.0003 atmosphere carbon dioxide, we would have (see p. 250) a maximum concentration of carbonate ions

 $C_{CO_3} = \frac{C_{8O_4}}{4,700} = \frac{0.0132}{4,700} = 2.8 \times 10^{-8}$ 

Then, according to equation 42 (p. 252) we must have sufficient calcium bicarbonate in solution to give a concentration of acid carbonate ions

$$C_{HCO_3} = \sqrt{\frac{3.04 \times 10^{-7}}{7.0 \times 10^{-11}}} \times 0.0003 \times 0.04183 \times 2.8 \times 10^{-6}$$

$$= 0.00039$$

and the concentration of the ionized calcium carbonate would be 0.000195 gram molecule. Its degree of ionization is 74 per cent, calculated by the method used before, so the total calcium bicarbonate in solution is 0.000264 gram molecule per liter.

¹ Chamberlin and Salisbury, Geology, p. 309.
² Kohlrausch and Holborn, loc. cit., p. 200. For 0.01 equivalent the degrees of ionisation are 63 and 65 per cent respectively.
² Page 250.
⁴ In this calculation we are not including a study of the effect of sodium chloride, but are limiting ourselves to an examination of the effect of sulphates alone in an aqueous solution. It is understood that the calculations are only for a rough orientation, the simplicity of the laws for dilute solutions being lost as solutions become more concentrated and more complex. Vide also E. C. Sullivan, Journal of the American Chemical Society, 27, 529 (1905).

If such a solution is now allowed to evaporate under a partial pressure of 0.0003 atmosphere of carbon dioxide to one-quarter its original concentration, we should have left a solution containing approximately 0.08 gram molecule of sulphates per liter, whose degree of ionisation may be taken as 39 per cent. Then  $C_{80} = 0.08 \times 0.39 = 0.0312$ 

and the maximum concentration of carbonate ions would be

$$C_{CO_8} = \frac{0.0312}{4700} = 6.64 \times 10^{-6}$$

Consequently

$$C_{HCO_3} = 0.00039 \times \sqrt{\frac{6.64}{2.8}}$$

and the concentration of ionized calcium bicarbonate is 0.0003 mole. Its degree of ionization is 63.4 per cent and the total concentration of calcium bicarbonate 0.00047 mole. Comparing this result with the original solubility of the bicarbonate (0.000264 mole), we find that while the solubility of the gypsum is decreased (see below) by the accumulation of the other sulphates, the solubility of the bicarbonate increases, in consequence of the decreasing concentration of the calcium ions.

The total original gypsum in solution was 0.0091 gram molecule per liter. By evaporation of the solution to one-quarter of its volume,  $C_{SO_4}$  has become 0.0312, and consequently

$$C_{Ca} = \frac{0.000059}{0.0312} = 0.0019$$

which we may consider as derived entirely from the ionization of the gypsum.

Its degree of ionization in a 0.08 molar solution of sulphates is about 39 per cent, and therefore the total concentration of the gypsum left in solution is about 0.0019/0.39 or 0.0049 gram molecule. A quarter of a liter would contain 0.0012 gram molecule, and therefore of the total original 0.0091 gram molecule 0.0079 gram molecule or about 90 per cent would have crystallized out. The weight of this would be 1.07 grams (calculated as calcium sulphate).<sup>2</sup>

The total original concentration of calcium bicarbonate was 0.000264 gram molecule, and we have left a quarter of a liter with 0.00047/4 gram molecule. Consequently, 0.000147 gram molecule or 0.0147 gram of calcium carbonate should be deposited with 1.07 grams of calcium sulphate, corresponding to a contamination of 1.37 per cent.

A further evaporation to one-eighth of the original volume should deposit according to similar calculations 0.101 gram calcium sulphate with 0.0047 gram calcium carbonate, representing 4.7 per cent.

With a partial pressure of 0.00003 atmosphere of carbon dioxide the original solubility of the bicarbonate would be  $8.3\times10^{-6}$  moles. By concentration of 1 liter to one-quarter of a liter, the solubility would be increased

<sup>&</sup>lt;sup>1</sup> The degree of ionization of magnesium sulphate, the chief sulphate left.
<sup>2</sup> During the evaporation to one-half liter, we should expect a deposit of 0.72 gram sulphate with 0.0104 gram carbonate or 1.44 per cent. carbonate would be present.

to  $14.8 \times 10^{-6}$  gram molecule per liter and only 0.0046 gram of calcium carbonate would be deposited with 1.07 grams of calcium sulphate crystallizing out as gypsum by the concentration, representing a contamination of 0.43 per cent.

With a partial pressure of 0.003 atmosphere of carbon dioxide the original solubility of calcium bicarbonate would be 10 times as great as in the case just discussed, amounting therefore to  $8.3 \times 10^{-4}$  moles. Evaporation of the solution to one-quarter its volume would increase the solubility to  $14.8 \times 10^{-4}$  gram molecules per liter and 0.046 gram of calcium carbonate would be deposited with 1.07 grams of sulphate, representing 4.3 per cent.

The results are summarized in table 6.1

TABLE 6.

CO <sub>2</sub> (atmos.).	CaSO <sub>4</sub> (grams).	CaCO <sub>2</sub> (gram).	CaSO <sub>4</sub> (mole).	CaCO <sub>2</sub> (mole).	Per cent CaCO <sub>3</sub> .
0.00003	1.24	0.0083	0.0091	0.000083	0.44
.0003	1.24	.0264	.0091	.000264	1.43
.003	1.24	.083	.0091	.00083	4.40

Column 1 gives the carbon-dioxide pressure in atmospheres; column 2 gives the weight in grams of calcium sulphate in 1 liter; column 3 the solubility of calcium carbonate and bicarbonate (expressed in grams of calcium carbonate); columns 4 and 5 give the values of the two previous columns in moles per liter. The last column gives the contamination of gypsum with sodium carbonate (referred to dehydrated gypsum) produced by evaporation of three-quarters of the solution.

This table can be regarded only as a rough approximation, as it was not considered desirable to make more involved calculations at the present time, and certain factors modifying the results were therefore not considered, such as the change in solubility of carbon dioxide, the influence of the primary ionization of potassium sulphate, etc. It suffices, however, as an orientation as to the effect of the presence of sulphates on the probable contamination of gypsum with calcium carbonate: the decreased solubility of gypsum in the presence of such sulphates, allowing the calcium bicarbonate to dissolve more nearly as it does in the absence of gypsum, would increase the tendency to contamination of the gypsum and so a perfectly pure or exceedingly pure gypsum crystallizing under such conditions would a fortiori indicate a very low partial pressure of carbon dioxide.

¹ The calculations involve no greater total concentration than about 0.08 gram molecule total sulphates per liter (p. 257). Cameron and Seidell, Journal of Physical Chemistry, 5, 650 (1901), have determined the solubility of gypsum in the presence of sodium sulphate and found that 0.1 gram molecule sodium sulphate at 22° reduces its solubility from 2.1 grams calcium sulphate to 1.4 grams, which is qualitatively in accordance with the above calculations. No attempt was made by them or by the author to determine to what extent the ion product for calcium sulphate remains a constant in these determinations. In more concentrated solutions of the sodium sulphate, as Cameron and Seidell point out, double salt formation increases the solubility of the gypsum.

## CALCIUM SULPHATE, CARBONATE, AND BICARBONATE IN THE PRESENCE OF SODIUM CHLORIDE.

In both the previous cases discussed it was found that the absence of calcium carbonate in gypsum crystallizing from solutions containing calcium carbonate in equilibrium with the carbon dioxide of the air would be considered an indication of a very low partial pressure of the carbon dioxide. Even if the great mass of the excess of calcium carbonate in solution were deposited first, in the same locality or elsewhere, before the point of saturation for gypsum were reached, the requirements for equilibrium would be such as to keep so much of the carbonate in solution as to form an easily discernible contamination of the gypsum formed by further concentration.

In nature the crystallization of gypsum is supposed to occur usually by the concentration of waters containing a large excess of other salts, notably of sodium chloride, and the last question we shall try to consider now is the effect of sodium chloride on the conditions discussed in the preceding parts.

A salt like sodium chloride which has no ion in common with gypsum should, according to the law of mass-action, increase the solubility of the latter up to a certain point; the chloride and sulphate must react to a considerable extent to form calcium chloride and sodium sulphate:

$$CaSO_4 + 2NaCl = CaCl_2 + Na_2SO_4$$

As the ionization of the new salts in moderately concentrated solutions is by no means complete, considerable amounts of calcium and sulphate ions must be suppressed to form these salts in non-ionized form, and this would lead to an increased solubility of calcium sulphate according to equation (35), page 250. In fact, a rough calculation of the result of Cameron's determination of the effect of sodium chloride in 0.017 molar solution on the solubility of gypsum, made with the aid of Arrhenius's principle of isohydric solutions, led to a value for the ion or solubility product for calcium sulphate

 $C_{C_0} \times C_{SO_4} = 9.5 \times 10^{-4}$ 

in the presence of the salt, as compared with  $6.5\times10^{-6}$ , the value of the solubility product at 23° in the absence of salt.

For concentrated salt solutions the conditions, as is always the case, become more and more complex; we are more likely to have complex ions, such as NaSO<sub>4</sub>, and double salts formed in large quantities and leading not so much to abnormal changes in solubility as to changes which we have no means of estimating at present.<sup>2</sup> Cameron, however, has given us a large amount of empirical data which will be useful for the consideration of our subject. In regard to gypsum and sodium chloride<sup>1</sup> he finds the solubility of the former is rapidly increased, rising from 2.37 grams calcium sulphate (0.0174 mole) per liter to 7.50 (0.0555 mole) in the presence of 130 grams of sodium chloride, after which there is a gradual decrease in

Loc. cit., 5, 560.
 As to the lowering of solubility of the non-ionised calcium sulphate in salt solutions, comparable with the decreased solubility of carbon dioxide, see pp. 237, etc.

solubility again, which Cameron ascribes to the condensation of the solvent in aqueous solutions of electrolytes.1

Entirely analogous effects must be anticipated for the action of sodium chloride on calcium carbonate and bicarbonate, their ions also being suppressed, for instance, according to

$$Ca(HCO_2)_2 + 2NaCl = CaCl_2 + 2Na(HCO_2)$$

calcium chloride and sodium chloride being formed in considerable quantities according to the principle of isohydric solutions.3

Again, the molecular solubility of calcium carbonate is liable to be decreased, as was discussed for the sulphate, and we have in this case also the fact that the solubility of carbon dioxide is considerably less in salt solutions than in pure water, and this decreased solubility will reduce the amount of bicarbonate dissolved approximately proportionately to the cube roots of the change in the coefficients of absorption. So we have forces tending to increase the solubility as well as such as tend to decrease the solubility of calcium carbonate. As a matter of fact, Cameron found that at 25° for calcium carbonate and bicarbonate in equilibrium with air,4 the solubility was increased from 0.1046 gram bicarbonate per liter to 0.2252 gram by 51 grams (0.87 mole) sodium chloride, and then it was decreased by additional sodium chloride. There is, therefore, at first an increase in solubility and then a decrease, exactly as for gypsum. The characteristic bend in the curve occurs earlier than in the case of gypsum, which was to be expected, as the molecular solubility of carbon dioxide is also affected in this case.

Cameron s also determined the effect of sodium chloride on the solubilities of calcium sulphate, carbonate, and bicarbonate simultaneously, i.e., in mixtures in equilibrium with solid gypsum, solid calcium carbonate, and the air. This is the work that is of most interest and importance for us, and as we shall use the data the table is reproduced here (table 7).

TABLE 7.

	CaSO <sub>4</sub> (grams).	CaSO <sub>4</sub> (mole).	Ca (HCO <sub>3</sub> ) <sub>2</sub> (gram).	Ca(HCO <sub>3</sub> ) <sub>2</sub> (mole).	NaCl (grams).	NaCl (moles).
1	1.9298	0.0143	0.0603	0.000375	0	0
2	2.7200	.0201	.0724	.000450	3.628	0.0625
3	3.4460	.0255	.0885	.000550	11.490	0.1979
4	5.1560	.0381	.1006	.000625	39.620	0.6824
5	6.4240	.0475	.0603	.000375	79.520	1.3696
6	5.2720	.0390	.0563	.000350	121.900	2.0995
7	4.7860	.0354	.0482	.000300	193.800	3.3379
8	4.4620	.0330	.0402	.000250	267.600	4.6090

Loc. cit., 5, 576.

<sup>&</sup>lt;sup>2</sup> This ha s been shown to be reliable up to 0.4 normal solutions. (Summary by A. A.

This has been shown to be reliable up to 0.4 normal solutions. (Summary by A. A. Noyes, loc. cit.)

When no other calcium salt is present, the solubility changes according to the cube root of the concentration of the carbon dioxide (equation (30), p. 247). When another calcium salt, e.g., gypsum, is present in large excess, so that C<sub>Ca</sub> may be considered constant, the solubility changes approximately as the square root of the concentration of carbon dioxide (equation (25), p. 246, and (42), p. 252).

No mention is made as to the partial pressure of the carbon dioxide, whether "laboratory air" or pure country air was used.

Loc. cit., 5, 653.

We note, first, the interesting fact that the solubility of the calcium bicarbonate is very much reduced by the presence of the gypsum, as required by the theory developed above. Cameron did not report any experiments on the effect of a change in the partial pressure of carbon dioxide, but it will undoubtedly be entirely analogous to that discussed in the previous parts of this paper; it is probable that the solubility will increase roughly proportionately to the square root of the pressure of carbon dioxide.

We may now raise the question whether, owing to the displacement of the bend in the curve of the solubility of bicarbonate as compared with that of gypsum in the presence of sodium chloride, by a process of concentration gypsum would crystallize out of any of the above solutions free from carbonate, and if not what the contamination would be.

If we go from solution 2 to solution 3, the sodium chloride concentration is increased from 0.0625 to 0.1979 mole, which would result if 100 liters of solution 2 were concentrated to 31.54 liters of solution 3. Of the 272 grams of calcium sulphate in 100 liters of solution 2, 108.7 grams would be retained in solution and 163.3 grams deposited. At the same time, of the 4.5 grams calcium carbonate in solution (as bicarbonate), 2.77 grams would be deposited, that is 1.7 per cent referred to pure calcium sulphate.

Table 8 gives the results of the calculations of this effect of progressive concentration from solution 2, through solutions 3, 4, etc., to solution 8. In column 1 the number of the solution used is given, referred to the numbers in table 7. In column 2 the number of liters used for concentrating is given, and in the next column we have the number of liters to which the solution has been concentrated. Column 4 gives the weight in grams of calcium sulphate deposited, and the last column gives the proportion of calcium carbonate to anhydrous sulphate deposited.

TABLE 8.

Solution used.			Grams Ca8O <sub>4</sub> deposited.	Per cent CaCO <sub>8</sub> .
No. 2	100.00	31.54	163.3	1.7
No. 3	31.54	9.12	61.7	1.9
No. 4	9.12	4.54	17.8	2.3
No. 5	4.54	2.96	13.6	0.5
No. 6	2.96	1.86	6.7	0.7
No. 7	1.86	1.35	2.8	0.8

We see from table 8 that the most favorable point for the deposit of pure gypsum is in going from solution 5 to solution 6, which is the point where the curve of solubility of gypsum bends, its solubility now decreasing and a relatively large amount of it being deposited; the bend in the curve of the solubility of the bicarbonate has already been passed and there is now no corresponding increase in the formation of carbonate, this increase having occurred before and produced the strong contamination in the previous series.

<sup>&</sup>lt;sup>1</sup> See note 3, p. 260.

Nothing is stated in Cameron's paper whether the air used was "laboratory air" with an excess of carbon dioxide in it or pure country air.1 If laboratory air was used, the amount of calcium bicarbonate obtained in solution and subsequently precipitated would be excessive and the results in the last column of table 8 might be materially lower for air with a carbondioxide content of 0.0003 atmosphere.

It is interesting to note that according to Usiglio's 2 work on Mediterranean water, calcium sulphate began to be deposited when the water reached a density of 1.13. This corresponds to a chloride content of about 17 per cent, or about 3 gram molecules of sodium chloride per liter, a concentration reached in Cameron's experiments for solution 7, from which, going to solution 8, gypsum would be obtained with about 0.8 per cent car-At this concentration, the concentration of other sulphates is still so small that they would tend to increase the contamination with carbonate, as described above, rendering the calcium sulphate less soluble and the bicarbonate more so.

At a lower partial pressure of carbon dioxide than 0.0003 atmosphere, the proportion of carbonate would be reduced approximately in the ratio of the square roots of the ratios of the partial pressures, i.e., a partial pressure of only 0.00003 atmosphere would reduce the carbonate to about  $\frac{1}{5.16}$  parts of the values given in the last column of table 8, or to still less on the probable assumption that the experiments on which the table is based were not carried out with pure air, and would produce a very pure deposit.

#### THE EFFECT OF TEMPERATURE CHANGES.

Reliable data on the solubility of calcium carbonate at temperatures other than 16°, the temperature at which Schloesing's experiments were carried out, are not at hand, and so the effect of changes of temperature on the conditions we are studying can not be estimated. It may be pointed out, however, that aside from a probable increase in the solubility of calcium carbonate, a higher temperature would affect chiefly the solubility coefficient of carbon dioxide, and through it would reduce the formation of calcium bicarbonate. The solubility of gypsum is about the same at 50° to 65° as at 18° and ionization constants are usually not changed greatly by changes of temperature; but the coefficient of absorption 5 for carbon dioxide at 65.5° is just about one-ninth as large as the coefficient at 18°. This would result, according to equation (42), in reducing the formation of calcium bicarbonate to  $\sqrt{\frac{1}{6}}$  or one-third of the value found for 16°. words, a rise of temperature of some 50° would probably have about the same effect on the solubility of calcium bicarbonate as a decrease in the

<sup>&</sup>lt;sup>1</sup> Results obtained by McCoy (American Chemical Journal, 29, 461 (1903), in repeating other work of Cameron on conditions of equilibrium involving the carbon dioxide of the air and showing decided discrepancies, form a very strong indication that pure air was not used by Cameron.

<sup>2</sup> Encyclopædia Britannica.

<sup>3</sup> See note 3, p. 260.

<sup>4</sup> Comey, Dictionary of Solubilities, p. 422.

<sup>5</sup> Dammer, Handbuch der Anorganischen Chemie, 11, 1, p. 371.

partial pressure of carbon dioxide to one-ninth its present value. In view, however, of the unknown change of solubility of calcium carbonate (the change in the ion product constant), it must remain undecided whether a rise of temperature would be a favorable or an unfavorable factor in the crystallization of gypsum free from carbonate. The formation of bicarbonate would also be directly proportionate to the square root of the solubility constant according to equations (40) and (42).

## SUMMARY OF RESULTS.

(1) From Arrhenius's data on the solubility of silver acetate, valerate, and butyrate in the presence of the sodium salts of the same acids, it was shown that the solubility or ion products are approximate constants, as calculated on the basis of the well-established principle of isohydric solutions. This, with the results of others, removes the discrepancy existing in the relation between the solubility product and the ionization of strong electrolytes and gives us a safer empirical foundation for the consideration of the equilibrium conditions existing between two precipitates, one which is in harmony with the fundamental work of Guldberg and Waage.

(2) The second ionization constant of carbonic acid may be taken as  $7.0 \times 10^{-11}$  as calculated from McCoy's data with the aid of corrections sug-

gested but not carried out by the latter.

(3) The solubility product of calcium carbonate is found to be 1.26×10<sup>-6</sup> on the basis of Schloesing's experiments on the solubility of calcium carbonate at 16° under varying partial pressures of carbon dioxide.

(4) The solubility of calcium carbonate and calcium bicarbonate is approximately proportionate to the square root of the partial pressure of

carbon dioxide in the presence of a large excess of calcium sulphate.

(5) The theory of the equilibrium conditions between calcium sulphate and calcium carbonate and bicarbonate has been developed and may prove

useful in the study of the natural waters of the present day.

(6) Considering the results given in tables 5,<sup>2</sup> 6,<sup>8</sup> and 8,<sup>4</sup> we find that the favorable factors for the crystallization of pure gypsum should be:

(a) The absence of other sulphates which in moderate proportions render gypsum less soluble and consequently enable solutions to take up more calcium bicarbonate than pure aqueous saturated solutions of gypsum can dissolve.

(b) The presence of sodium chloride in the proportion of about 8 to 25 per cent.<sup>5</sup>

(c) A very low partial pressure of carbon dioxide, the solubility of calcium carbonate varying approximately as the square root of the partial pressure of carbon dioxide, according to (4).

pressure of carbon dioxide, according to (4).

(d) An increase of temperature by decreasing the coefficient of absorption of carbon dioxide would possibly, but not certainly, be a favorable factor, the formation of calcium bicarbonate being proportionate to the square root of the absorption coefficient of carbon dioxide, which falls with increase of temperature.

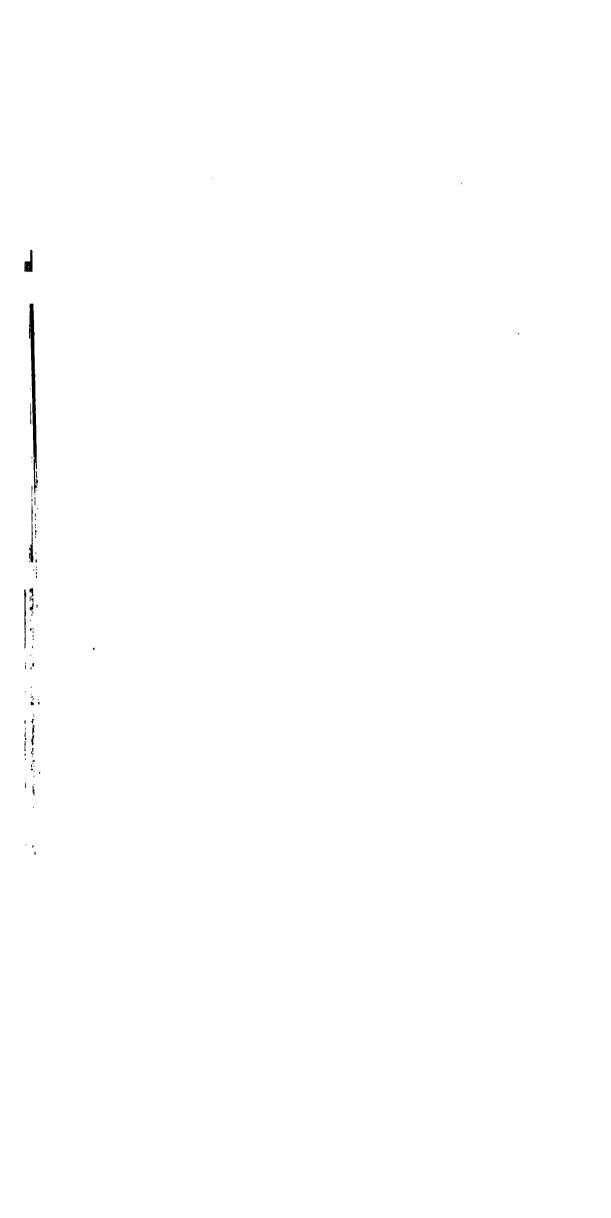
<sup>&</sup>lt;sup>1</sup> A. A. Noyes, *loc. cit.*; Findlay, *loc. cit.* <sup>2</sup> Page 254. <sup>1</sup> Page 258. <sup>4</sup> Page 261 <sup>5</sup> Solutions 5, 6, 7, table 7, p. 260.



It is conceivable that the conditions (a), (b), (c), and (d) should lead to a primary deposit of exceptionally pure gypsum, especially when acting jointly. The considerations developed make it desirable to examine such and other deposits of gypsum very carefully and exactly for even very small quantities of carbonate.

(7) Even if the great mass of an excess of calcium carbonate in a solution were deposited first in some other locality before the point of saturation for gypsum were reached, the requirements for equilibrium would be such as to hold carbonate in solution and to make the question of the place of deposit of the excess of carbonate in the first instance one of no moment.





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