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SIR DAVID BREWSTER, K.H. LL.D. F.R.S.L. & E. &c.
SIR ROBERT KANE, M.D. F.R.S. M.R.I.A.
WILLIAM FRANCIS, Ph.D. F.L.S. F.R.A.S. F.C.S.

"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster
vilior quia ex alienis libamus ut apes." Just. Lips. *Polit.* lib. i. cap. 1. Not.

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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua . . . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

—" Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas;
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

CONTENTS OF VOL. XXXV.

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NUMBER CCXXXIV.—JANUARY 1868.

NUMBER CCXXXV.—FEBRUARY.

NUMBER CCXXXVI.—MARCH.

NUMBER CCXXXVII.—APRIL.

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NUMBER CCXXXIX.—JUNE.

PLATES.

Berthelot's New Thermometer
for measuring temperatures above the Boiling
Point of Mercury.

Fig. 2.

Fig. 1.

I. *On the Theory of Phlogiston.*
By George Farrer Rodwell, *F.C.S.*[*]

I. Of the "*subtilis ignis*" of the Ancients.—II. Of old chemical literature, and of the significance of the terms *Sal, Sulphur, Mercurius,* as employed by mediæval Chemists.—III. Of the supposed nature of fire prior to the rise of the theory of Phlogiston; specially of Descartes's *materia cœlestis,* and of Hooke's theory of combustion.—IV. Of the ideas regarding the calcination of metals which prevailed prior to the rise of the theory of Phlogiston.—V. Of Becher and Stahl, and of the rise and development of the theory of Phlogiston.—VI. Of the syncretistic nature of the theory of Phlogiston.

THE theory which proposed to trace the cause of various phenomena of chemical change to the absorption or rejection of "*materia aut principium ignis, non ipse ignis,*" (commonly called the *theory of Phlogiston*), although much talked of, is, I venture to assert, but imperfectly understood in its entirety. It is valued because it was adopted by many notoriously eminent chemists of the last century; it is applauded because the phlogistians elaborated it into a comprehensive system, and in so doing paved the way for our modern science; it is respected because we are taught to believe that it was the first chemical theory, and the more ardent theorizers of our day point to it triumphantly as an example of the good which may be effected even by a false and chimerical theory. I have endeavoured in the following pages to show to what extent we are justified in our present estimate of the theory.

[*] Communicated by the Author.

Phlogiston was not a new creation; possessing other names, and endued with ill-defined and varying functions, it had been conspicuous in many physical systems. The chief merit of Becher and Stahl was that they extended its functions in one direction, and conferred upon them a definitiveness which they had hitherto lacked. The theory of phlogiston was not the result of a sudden development, it did not owe its existence to an intellectual exploit, but it arose by a process of evolution, and by a gradual modus of development.

Let us trace the course of that development.

I. *Of the* "subtilis ignis" *of the Ancients.*

The earliest physical theory of which we have any cognizance, affirmed that the universe consists of four elements—fire, air, water, and earth. We have good evidence that this theory prevailed prior to the fifteenth century B.C.; indeed it seems probable that it originated before the separation of the Medo-Persic and the Hindu branches of the Aryan family. Zoroaster appears to have introduced element-worship among the Medo-Persic races, and as he is supposed to have been a Scythian, it is probable that this form of worship originated with the Scyths. In the ancient Brahmanical religion three gods, symbolized by elements, were worshipped, and first in this trinity was Agni, the god of fire. But while the Hindus adopted a polytheism, the primitive Magism introduced by Zoroaster was developed into a monotheism, and as fire was considered first and most potent of the elements, it became the one visible symbol of their god. The divinity was called "the one fire," "the first fire," from whom proceeds "$\zeta\omega\eta\phi\acute{o}\rho o\nu\ \pi\hat{v}\rho$," which diffuses itself through all matter, and penetrates to the centre of the earth. It was believed to be the principle of life; and the soul was regarded as a very pure fire, indestructible, and eventually returning to the original "first fire"—

"ὅτι ψυχὴ πῦρ δυνάμει πατρὸς οὖσα φαῖνον
ἀθάνατός τε μένει, καὶ ζωῆς δεσπότις ἐστί"*.

This belief pervades later philosophy. Thus Aristotle affirms that some derive ζῆν from ζέειν because the soul is heat:—"Οἱ μὲν τὸ θερμὸν, λέγοντες ὅτι διὰ τοῦτο καὶ τὸ ζῆν ὠνόμασται"†. Seneca says, "Nihil enim viveret sine calore"‡.

The potency of the Zoroastrian divinity was proved in the

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* *Vide* Πατρικίου τὰ τοῦ Ζωροάστρου λόγια.

† Περὶ Ψυχῆς, lib. i. cap. 2.

‡ *Quæst. Natur.* lib. ii. cap. 10.

one direction by the destructive power of fire (his visible manifestation), and in the other by its beneficent and life-cherishing attributes in the gentler form of solar light and heat. But the first was not always an efficient proof; for Suidas relates that on one occasion, when the Chaldæans sought to prove that their god was greater than Canopus, a priest of the latter filled the image of his god with water, having previously bored holes in it, which were stopped up with wax. " The Chaldæans began the contest with much rejoicing, and put fire round about the statue; the wax melted, the holes opened, and water gushing forth put out the fire; hence the Chaldæans were laughed at for their god "*. We trace some analogy with the Chaldæan practice in the account of Elijah and the priests of Baal.

The Greek philosophers adopted the four-element theory, and they assigned a relative order of occurrence to the elements. Thus fire was considered the most subtle, and it occupied the highest place; next in order came air, then water, and finally earth, most gross and occupying the lowest place. Fire and air, they said, are light; water and earth heavy. All fire has a tendency upwards because it seeks to join that which is above all; all earth has a tendency downwards because it seeks to join its elemental mother. Special prominence was given to one or other of the elements by different philosophers. Thus Thales maintained that water was the primal element (a theory which was adopted in some of the later systems, notably in that of Van Helmont, and partially in that of Becher); Anaximenes considered air the primal element, while Hippasus the Pythagorean, and his disciple Heraclitus, gave the prominence to fire. This we can well understand when we remember that Pythagoras drew somewhat largely from Chaldaic sources; indeed his philosophy is plainly tinctured by some of the Zoroastrian tenets. Zeno held that there are two kinds of fire,—the one, common artificial fire, which requires nutriment; the other, " ἀτεκνεκον πῦρ," the subtle elemental fire sustaining all things. This latter he affirmed is diffused throughout the universe : even the coldest bodies possess it ; for very cold water can be made colder, and then becomes ice. The distinction would thus seem to have been applied by Zeno between fire manifesting itself by phenomena of light and heat, and the heat which is associated with all substances, the presence of which can only be proved by artificial conditions. This idea of the existence of two kinds of fire was very generally adopted in after times; and, as we shall presently see, it forms the basis of the theory of Phlogiston. Chrysippus, a follower of Zeno, considered fire the active principle of the

* Stanley's ' History of Chaldaic Philosophy.'

world, because it alone of the elements possesses innate motion. Lucretius, who followed Epicurus very closely, asserts that lightning is elemental fire, consisting of smaller atoms than our earthly fire, and hence more subtle and capable of greater penetration[*]. The pure fire was distinguished by various names— among others, "*subtilis ignis*," "*cœlestis ignis*," "*tenuis ignis*," as opposed to "*common fire*," "*mundane fire*," "*gross earthly fire*," &c. From a passage in the 'Νεφέλαι' of Aristophanes, it would appear that the ancients were in the habit of obtaining their "mundane fire" from "celestial fire" by means of a burning-glass[†]; but the distinction would still seem to exist, for the pure fire would only become visible earthly fire when associated with some combustible substance. According to Seneca, the Egyptians somewhat extended the four-element theory by assigning to each element a masculine and feminine, an active and a passive form : thus air was divided into active wind and passive atmosphere ; fire into active flame and comparatively passive light[‡].

Aristotle is believed to have been the first to add a fifth element, more divine than the others—*αἰθὴρ*, the æther, pervading all things, and in perpetual motion. He asserts that it gives motion to the other elements, and hence derives the term from *ἀεὶ* and *θέω*. The term *quinta essentia*, afterwards employed by the chemists, originated from this idea of a fifth element. A subtle medium, rarer than air, was admitted in ancient Hindu philosophy ; we find it alluded to both in the Sanch'ya and

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[*] " Perfacile est jam animi ratione exsolvere nobis
         Quare fulmineus multo penetralior ignis
         Quam noster, fluat, e tædis terrestribus ortus.
         Dicere enim possis cœlestem fulminis ignem
         Subtilem magis e paruis constare figuris :
         Atque ideo transire foramina quæ nequit ignis
         Noster hic e lignis ortus, tædaque creatus."
                    De Rerum Natura, lib. ii.

[†] STREPSIADES.   ἤδη παρὰ τοῖσι φαρμακοπώλαις τὴν λίθον
             ταύτην ἔωρας, τὴν καλήν, τὴν διαφανῆ,
             ἀφ' ἧς τὸ πῦρ ἅπτουσι;
  SOCRATES.   τὴν ὕαλον λέγεις ;
  STREPSIADES. ἔγωγε.
  SOCRATES.   φέρε, τί δῆτ' ἄν;
  STREPSIADES.   εἰ ταύτην λαβὼν,
             ὁπότε γράφοιτο τὴν δίκην ὁ γραμματεὺς,
             ἀπωτέρω στὰς ὧδε πρὸς τὸν ἥλιον,
             τὰ γράμματ' ἐκτήξαιμι τῆς ἐμῆς δίκης."

[‡] " Ægyptii quatuor elementa fecere : deinde ex singulis bina marem et feminam. Aërem marem judicant, qua ventus est ; feminam qua nebulosus et iners. Aquam virilem vocant mare ; muliebrem omnem aliam. Ignem vocant masculum qua ardet flamma, et feminam qua lucet innoxius tactu. Terram fortiorem marem vocant, saxa cautesque ; feminæ nomen assignant huic tractabili ad culturam."—*Quæst. Natur.* lib. iii. cap. 14.

Nyaya systems; and it appears probable that it was recognized as a fifth element prior to the year 900 B.C. It was believed to be all-pervading; and its special quality was, that sound originates from its motion, and is transmitted by it.

In considering the application of the four-element theory, we must bear in mind that the elements were not viewed in their strictly literal sense; it was not believed that there is but one kind of fire, air, water, and earth. Light, the heat inherent in all bodies, flame, incandescent bodies, together with lightning and all visible manifestations of electricity, were included with the element *fire**. Smoke, steam, and whatsoever appertained to gaseity, were included with *air*. Blood, milk, and wine (the most familiar liquids after water to the early races) were included with *water*. Finally rocks, cultivable land, and metals (essentially different in the eyes of the most primitive man) were included with the element *earth*. The four elements were types of great classes which together comprised the universe; in an extended sense they typified *solidity, liquidity,* and *gaseity,* while fire represented the *force* exercising itself upon matter. The function of fire is well signified in the story of Prometheus. Fire was the *anima*; air, water, and earth together constituted the *corpus*. A rude classification of this description must of necessity obtain, until, by means of refined methods of observation and a determinate modus of physical thought, minuter differences can be detected and examined, until by various tortures we can force nature to yield up her well-concealed secrets; for, as Francis Bacon has observed, " occulta naturæ magis se produnt per vexationes artium, quam cum cursu suo meant "†. Let us bear in mind, if we are disposed to harshly criticise the four-element theory, that although instituted in barbaric times and by unlettered men, it prevailed universally during the most golden period of ancient philosophic thought, and very generally during the Middle Ages and the succeeding period; even in the memory of our grandfathers the idea was not utterly subverted.

II. *Of old chemical literature, and of the significance of the terms* Sal, Sulphur, Mercurius, *as employed by mediæval Chemists.*

I say the four-element theory obtained *very generally* during the Middle Ages, because it did not obtain universally; for there had arisen a sect of men who devoted themselves to the study of the intimate nature of matter, and who had elaborated

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* Plato speaks of the various kinds of fire in the *Timæus*; and Aristotle has the following passage :—" Οὐ γάρ ἐστιν ἐν εἶδος τοῦ πυρός· ἕτερον γάρ ἐστι τῷ εἴδει ἄνθραξ, καὶ φλὸξ, καὶ φῶς, ἕκαστον αὐτῶν πῦρ ὄν."

† *Novum Organum,* lib. i. aph. 98.

a mode of thought different from that which had prevailed at any prior period : these were *the Chemists.* Whatever their ultimate object may have been (alchemy, iatro-chemistry, metallurgic chemistry), their immediate pursuits led them to study the structure of matter, the varying nature of different kinds of matter, and the modus of their change under the most artificial and forced conditions which could be commanded. Rejecting the four-element theory as expressed by the ancients, the chemists adopted three principles, which they designated *sal, sulphur, mercurius,* and before we go further it is important for us to understand accurately the right significance of these terms. It is not unfrequently imagined that they are to be taken in their literal sense ; but no idea can be more erroneous, or more likely to lead to false impressions as regards the early history of chemistry. The terms were used exactly as we now use the term *alkali* or *salt* in chemistry ; not one alkali, not common salt, but all bodies possessing certain qualities in common, and taking their name from the first known of their class, or from some dominant quality which they possess in common. The *salt, sulphur,* and *mercury* of the chemists are "*principia,*" not "*corpora;*" they are " ἀνάλογα "—representative bodies, types of classes, types of qualities ; by them is expressed in other terms the fire, air, water, and earth of the ancients. *Fire* is included under the term *sulphur*—the principle of combustibility. *Air* and *water* (liquidity and gaseity) are included under the term *mercury*—the principle of volatility. Finally, *earth* is included under the term *salt*—the principle of fixity and solidity.

Empedocles adduced a simple experiment in support of the four-element theory : he burnt wood, and pointed out the presence of the elements :—visible *fire*; *air* represented by the smoke ; *water* exuding from the charring wood ; and *earth* remaining on the hearthstone in the form of ash. The chemists as readily proved the presence of their three elements :—the combustible flame-generating part of the wood they said is *sulphur,* the volatile part is *mercury,* the ash is *salt.* Paracelsus says, very concisely, " For whatsoever fumes and evaporates in the fire is *mercury* ; whatsoever flames and is burnt is *sulphur* ; and all ash is *salt*"*.

Beguinus, in his famous *Tyrocinium Chymicum*†, has extended

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* *De Rerum Natura,* lib. vi.

† This work was published in Paris in 1615, and was reprinted in various parts of Europe in 1618, 1624, 1637, 1650, 1665, and 1669. The above is extracted from the 1669 edition, which was published simultaneously with Becher's *Physica Subterranea.* This edition is elaborately paraphrased by Gerard Blasius, assisted by the writings of twenty-seven of the most eminent chemists who had preceded him.

the physical theory very fancifully and somewhat metaphysically ; it will be observed, however, that the inception of the extension tends to confirm the view expressed above :—

Sal.	*Sulphur.*	*Mercurius.*
Sal commune.	Sal petræ.	Sal ammoniacum.
Acerbum et amarum.	Dulce.	Acidus.
Corpus.	Anima.	Spiritus.
Materia.	Forma.	Idea.
Patiens.	Agens.	Informans aut movens.
Ars.	Natura.	Intelligentia.
Sensus.	Judicium.	Intellectus.
Fixum.	Inflammabile.	Vaporosum.
Vinculum.	Calidum.	Humidum nativum.
Materiale.	Spirituale.	Gloriosum.

The salt, sulphur, and mercury classification, even in its least extended sense, appears somewhat far-fetched ; but I think it is demonstrable that there is a certain appropriateness about it. *Salt* has in every age been one of the most familiar solids, and on account of its homogeneity and fixity in the fire we can quite understand that it appeared to the old chemists the nearest approach to a pure solid ; hence it was taken as the type of solidity. *Sal* was more definite and tangible than the broad term *terra* ; and for obvious reasons neither a metal, nor one kind of rock, nor cultivable earth, could be taken as a type of solidity : indeed salt was the most elemental definite solid that was then recognized, simply because there was no means of revealing its compound nature, while the really elemental metals could be apparently proved to be compound. *Mercury* (synonymous with the Greek ʽΕρμῆς) has in every age been the symbol of activity and volatility ; and the chemists had an additional reason for adopting the term, because they traced the origin of their science to the mythical Hermes (or, as they frequently call him, Mercurius) Trismegistus. In some of the old chemical works we find the terms used indiscriminately ; thus " our volatile Hermes " would denote a product of distillation, and be otherwise expressed as " the mercury " of the body distilled. The " sideric mercury " of Paracelsus was supposed to receive its powers from the stars, and to confer fluidity and volatility upon bodies.

It is, however, to the third element (*sulphur*) that we must specially direct our attention. Sulphur was peculiarly fitted to be the representative of combustibility ; it was the most abundant readily combustible body known, and from an early age had been intimately connected with the element fire. If we might accept the usual derivation of the word (sal πῦρ*), it would seem to show that it was regarded as *the* combustible substance

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* This appears to have been proposed by Isidorus ; vide *Vossii Etymologicon Linguæ Latinæ,* 1664, and elsewhere.

par excellence; but Professor Max Müller informs me that the word *sulphur* has no etymology in Latin, and is probably derived from a Sanskrit root. I may mention that sulphur was frequently called "lapis ardens," and was sometimes qualified by the word "πεπυρωμένον. "Assimilatur igni," says Beguinus, "propter flammam, quam facile concipit." Again, we know that at a far earlier period the connexion had been recognized; for both in the Pentateuch and Apocalypse we read of the destruction of cities, &c., being effected "πυρὶ καὶ θείῳ," or, as the Vulgate has it, "igne et sulphure," and, quite literally in our English version, "with fire and brimstone." A sulphurous smell accompanying lightning is frequently mentioned by ancient writers; and it seems probable that the Greek term θεῖον originated from this idea; for, since sulphur appeared to accompany divine manifestations, it would seem reasonable to designate it by a name indicating its origin.

Every combustible body was believed by the chemists to contain *a sulphur*, upon the presence of which its combustibility depended; hence the term "sulphureous" came to be applied instead of "combustible," and soon entirely superseded it. There were necessarily many *sulphurs*: thus there was "the sulphur of wood" (carbon), "the sulphur of wine" (alcohol), "the sulphurs of metals" (frequently actual sulphur), even "the sulphur of charcoal;" and, by a gross error (disproved by Boyle), "the sulphur of nitre" was specified; for when fused nitre was caused to act upon a combustible body, it was not at first observed that the nitre itself was incombustible. Boyle describes the inflammable "fume" which is given off when acid is poured upon iron-filings as consisting of "the volatile sulphur of Mars, or of metalline steams participating of a sulphurous nature"*. Thus inflammable solids, liquids, and gases were alike called *sulphurs*. If more be needed to show that by the term sulphur the chemists signified a combustible principle, let me quote a passage from a work published during the lifetime of Becher, and written by an author whom he not unfrequently quotes. Boyle, in a treatise 'On the Producibleness of Chemical Principles,' published in 1680, speaks of "the sulphur of the chemists" in the following terms:—"But because the most intelligible and least indefinite notion their writings suggest of sulphur is that 'tis a combustible and inflammable principle, I have hitherto treated of it as such." The same idea was attached by Paracelsus to his "*sideric sulphur*," which he supposed to receive its influence from the stars, and to possess the property of conferring combustibility upon bodies.

* *Vide* his essay 'On the Difficulty of preserving Flame without Air,' published in 1672.

If we translate *sal, sulphur, mercurius* respectively as *principle of solidity, principle of combustibility,* and *principle of volatility* (excepting of course those instances in which the substance is directly specified, as mercurius in the account of the preparation of "mercurius præcipitatus per se," or sulphur in the preparation of "oleum sulphuris per campanum"), a good deal of the obscurity will be found to disappear from old chemical treatises. Let me, however, say at once that much of their obscurity never can disappear; it is inherent in them; the chemists purposely adopted it and delighted in it; a profound secret they said should not be revealed in the vulgar tongue, the true adept could sufficiently comprehend the mystical language, and it would not be right that it should be understood by the common people.

The works of the old chemists are for the most part characterized by an uncouth jargon, a studiedly fantastic phraseology, and a barbarous Latinity quite without precedent, except in the case of coexistent works on astrology. They abound in literal gibberish, and Geber was not unfrequently out-Gebered by his successors. The principal cause of the occult nature of old chemical works is to be traced to the fact that the authors of them frequently practised astrology; hence the obscurity which had been introduced into the one class of writings soon found its way into the other. Alchemy, astrology, divination, indeed Kabbalism generally may be classed under the same head; the same tone of thought is essential for the nurture of each. They were children of one parent; and although astrology had the start of her sisters, they long dwelt under the same roof, and were subject to the same influences; together they prevailed; together they were persecuted; together they fell. Of both may be said with equal justice, "ars sine arte, cujus principium mentiri, medium laborare, et finis mendicare." The astrologer and the alchemist pursued their callings under very similar conditions. Compare them as depicted by some of the old painters, we have but to replace the astrolabe by the alembic, and the change is effected—the same dull dingy cell, the same grey-headed wizened old man, the same great clasped volumes full of hieroglyphics, and the ever consumption of the midnight oil. Paracelsus, in comparing the chemist with the physician of his day, has given us the following account of the former :—" For they are not given to idleness, nor go in a proud habit, or plush and velvet garments, often showing their rings upon their fingers, or wearing swords with silver hilts by their sides, or fine and gay gloves upon their hands, but diligently follow their labours, sweating whole days and nights by their furnaces. They do not spend their time abroad for recreation, but take delight in their laboratory. They wear leather garments with a pouch, and an apron where-

with they wipe their hands. They put their fingers amongst coals, into clay and ordure, not into gold rings. They are sooty and black like smiths or colliers, and do not pride themselves upon clean and beautiful faces"*.

We still possess in the science of chemistry traces of the connexion which once existed between alchemy and astrology ; for the symbolic notation of chemistry undoubtedly originated from the profuse system of symbolization employed in astrology. The Chaldæans at a very early period designated the stars by signs ; and the number gradually increased until astrological works became one mass of symbolism. The sun, moon, and principal planets were among the first to receive symbols ; and before the time of Geber the seven metals were designated by the same names and symbols, and each star was supposed to directly influence the metal which bore its name. To a certain extent this was appropriate ; for what could better represent the sun than gold, or the moon than silver ? The nimble Mercury would naturally fall to argentum vivum, while Saturn, with its adverse influence ("malevolus et malitiosus"), would find a fitting representative in lead, the most despised of metals. By an enlargement of the idea the direct influence of the sun was supposed by some to be necessary for the work of transmutation ; hence we read of endeavours to effect " *the fixation of Sol,*" viz. the occlusion of the qualities supposed to exist in sunbeams in various base metals, which operation, once effected, thenceforth aurified them for ever. Symbols having been once introduced into chemistry, the practice spread ; a number of substances, together with chemical operations, and even vessels, were so designated, and long before the time of Dalton an extensive symbolic system prevailed. In the Vienna library there is a Greek manuscript, entitled "Κλεοπάτρας χρυσοποιία," which abounds with symbols, and which there is every reason to believe was written before the time of Geber. There can be no doubt that there were many writers on chemistry before the time of Geber, who lived in the eighth century of our era. In an unpublished MS. written by Antonio Neri, certainly before the year 1613, I find mercury designated by no less than thirty-five different names and twenty-two symbols, lead by sixteen names and fourteen symbols, and sulphur by two names and sixteen symbols. The following example (from Sir Kenelm Digby's ' *Chemical Secrets,*' published in 1683) illustrates the manner of employing symbols in the time of Becher :—" Take good mineral ☿ , mortifie it with radicated vinegar ; then seperate its quintessence with pure S.V. ; with that quintessence dissolve ☿ duplicatum of ☿ , that both become an oyl, which unite with a subtle calx of ☉,

* *De Rerum Natura,* lib. viii.

and bring them to an incombustible oyl, which will transmute ☿ into ☉." Sometimes a word was compounded of a symbol with the addition of letters, and was declined by the addition of the case-terminations to the symbol; thus, to take sulphur, 🜍 :—N. 🜍; G. 🜍 is; D. 🜍 i; A. 🜍 em; V. 🜍; Abl. 🜍 e. It is obvious that this could only be done with words which increase in the genitive; but the symbol was often otherwise applied, and (itself denoting a substantive) was made part of an adjective: thus the symbol for sal with *inus* added would signify *salinus*; the symbol for aqua with *tilis* added would signify *aquatilis,* and so on. It is some satisfaction to know that this barbarous custom never became very general. The following example is from the first part of Stahl's *Fundamenta Chemiæ*:— " Facilius solvitur ille nexus ⊖ini hujus et ▽ ei concreta per alcalia ⊖ia; subtilius per volatilia ☐osa; grossius per fixa incinerata, solutioni ⊙inis eadem soluta sub ♎ et olei per deliquium nomine instillando."

It is a sheer waste of time to read even the most celebrated treatises of the old chemists: the obscurity of one is reproduced in all; moreover they are excessively prolix; and if they do contain anything of interest, it is so buried in a mass of utterly irrelevant matter that it is scarcely worth the labour of extracting. I give below a few extracts from typical chemical works, and I do not apologize for the digression; for while it indicates the character of old chemical literature, it also gives us an insight into the condition of chemistry prior to the time of Becher, without the knowledge of which we cannot judge fairly of the theory of phlogiston, or of the manner of its evolution.

Let us, in the first place, hear the opinions of Basil Valentine[*] concerning the generation of metals, as expressed in his famous *Currus Triumphalis Antimonii* :—" Therefore think most diligently about this; often bear in mind, observe, and comprehend that all minerals and metals together in the same time, and after the same fashion, and of one and the same principal matter, are produced and generated. That matter is no other than a mere vapour, which is extracted from the elementary earth by the superior stars as by a sydereal distillation of the macrocosm ; which sydereal hot infusion with an airy sulphureous property descending upon inferiors, so acts and operates, as in those metals and minerals is implanted spiritually and invisibly a certain power and virtue, which fume afterwards resolves itself in the earth into a certain water, from which mineral water all metals are thenceforth generated and ripened to their perfection, and thence pro-

[*] Born 1394, wrote about 1415.

ceeds this or that metal or mineral, according as one of the three principles acquires dominion, and they have much or little of sulphur and salt, or an unequal mixture of them; whence some metals are fixed, that is, constant and stable; some volatile and easily mutable, as is seen in gold, silver, copper, iron, lead, and tin."

Writers on alchemy adopted a more occult style even than the above, and often conveyed their views in the form of a parable. The following extract, referring to the transmutation of the six inferior metals into gold, is from the *Novum Lumen Chemicum* of Michael Sendivogius* :—" And there appeared unto me a great man, upon whose forehead was written the name of Saturn, and taking a vessel he drew ten parts of water, and took presently of the tree of the sun and put it in; and I saw the fruit of the tree consumed and dissolved like ice in warm water. I demanded of him, ' Sir I see a wonderful thing, water to be as it were of nothing; I see the fruit of the tree consumed in it with a most sweet and kindly heat, wherefore is all this?' But he answered me most lovingly; ' My son it is true this is a thing to be wondered at, but do not thou wonder at it, for so it must be. For this water is the water of life, having power to better the fruit of this tree, so that afterwards neither by planting nor grafting, but only by its own odour it may convert the other six trees into its own likeness.' "

Lastly, let us take a passage from the treatise *De Rerum Natura* of Paracelsus† :—" The life of metals is a secret fatness; .... of salts the spirit of aquafortis; .... of pearls their splendor; .... of marcasites and antimony a tinging metalline spirit; .... of arsenics a mineral and a coagulated poison. .... The life of all men is nothing else but an astral balsam, a balsamic impression, and a celestial invisible fire; an included air, and a tinging spirit of salt. I cannot name it more plainly, although it is set out by many names."

These extracts are typical of three distinct phases of old chemical literature. It is difficult to say which author is the least obscure,—perhaps Basil Valentine; but there is not much to choose between them, and we can only wonder how such masses of unintelligible matter ever came to be printed. We must bear in mind, however, that the tone of chemistry had considerably improved before the time of Becher, mainly through the labours of Boyle and Lemery. The ' Sceptical Chemist ' of Boyle‡ was very serviceable in lessening the obscurity of future works on chemistry. Glauber§, although he often indulges in obscure language, and speaks of his "aurum potabile" as capable of

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* Born 1566, died 1646.   † Born 1493, died 1541.
‡ Born 1626, died 1691.   § Born 1604, died 1668.

curing all diseases, and gives directions for the profitable extraction of gold from flints, did good service to the science. Nicholas Lemery, for the first time in the annals of the science, gave long courses of lectures. As it may be interesting to note the subject matter of chemical lectures delivered towards the end of the seventeenth century, I give below the matter of two of Lemery's lectures from a course of thirty-four :—

Lecture 15.
" The distillation of Sal Saturni.
The tincture of Mars, continued.
The revivification of Mercury.
The dissolution of Mercury for making corrosive sublimate."

Lecture 33.
" Ninth and last sublimation of the panacea.
The fixed salt of *Carduus Benedictus,* ended.
The distillation of roses.
Preparation for the distillation of vipers."

III. *Of the supposed nature of fire prior to the rise of the theory of Phlogiston; specially of Descartes's " *materia cœlestis,*" and of Hooke's theory of combustion.*

Epicurus regarded heat as an effluxion of minute spherical particles, which in virtue of their smallness and of their rapid motion insinuate themselves into the densest substances, and eventually disunite them by the rapidity of their motion. Fire is an intense heat. Cold is an effluxion of angular particles moving less rapidly than the heat-particles. Lucretius held that both the light and heat of the sun are the result of the rapid motion of " primary particles" *. Cardanus† to a certain extent adopted the views of Epicurus : he frequently speaks of " *motus ignis* " and " *motus caloris.*" Flame is " *aër accensus ;*" fire is heat " *in immensum auctus,*" and it penetrates everything on account of its rapid motion :—" Ignis enim calidissimus, tenuissimus, celerrimi motus, ac qui facile omnia invadat, et momento maneat solum." Robert Fludd, writing in 1617, affirms that heat is not the actual essence of light, " sed quasi ultimus ejus actionis effectus, immediate a materiæ motu profluentis "‡.

During the Middle Ages the elemental nature of fire was almost universally admitted, and the two kinds of fire (treated

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*   Principio persæpe leveis res, atque minutis
         Corporibus factas, celereis licet esse videre.
         In quo jam genere est solis lux, et vapor ejus,
         Propterea quia sunt è primis facta minutis :
         Quæ quasi truduntur, perque aëris intervallum
         Non dubitant transire, sequenti concita plaga.

† Born 1501, died 1576.   ‡ *De Macrocosmi Historia.*

of in Section I.) were distinguished from each other.   Francis Bacon was one of the first to deny the elemental nature of fire ; he asserts that it is "merely compounded of the conjunction of light and heat in any substance"*, and he elsewhere defines heat as a violent motion of the smallest particles of bodies, and light as a product of heat.   Telesius of Consenza asserted that heat is the cause of motion, cold of rest,—and that these incorporeal principles act upon passive matter, and by their mutual reaction produce all the phenomena of the universe.   This theory was adopted and somewhat extended by Campanella.   Athanasius Kircher, in his *Ars Magna Lucis et Umbræ*, affirms that ordinary fire is air caused to glow by the vehement collision of bodies, by the heat of which combustible matter is changed into flame†.

Descartes assumed that all matter originally consisted of square particles, which at the Creation were furnished with two kinds of motion, the one producing the revolution of each particle around its own centre, the other the revolution of groups of particles around a common centre.   During this revolution the angles of the particles became abraded by collision, and hence were produced three elements.   The first ("*materia cœlestis*," "*materia subtilis*," or "*materia primi elementi*") consists of the fine dust produced by the abrasion of the angles, and moves with greater velocity than the other elements.   The second ("*globuli secundi elementi*"), of which the atmosphere and everything between the stars and the earth is constituted, consists of the spheres which are produced by the abrasion of the square particles ; it moves with greater velocity than the particles of the third element.   The third ("*particulæ tertii elementi*"), of which the earth and all terrestrial bodies are formed, consists of particles which are neither square nor spherical, are partially rounded by abrasion, but retain some of their angles‡.   Fire consists of particles of the third element rapidly agitated circularly by the *materia cœlestis*§, which is in perpetual motion, and is the cause of all the motion in the universe.   *Light* is apparent without heat, as in the case of phosphorescent bodies, when the *materia cœlestis*

* *Novum Organum*, lib. ii. aph. 20.

† "Ignis igitur noster usualis nihil aliud est, quam aër ex vehementi duorum corporum collisione accensus, cujus ardore combustibilis materiæ fomes arreptus in flammam abit " (lib. i. cap. 1).   The order of the Vicar-General of the Jesuits (to which sect Kircher belonged), directing the printing of the *Ars Magna Lucis et Umbræ*, is dated December 18, 1644 ; it was therefore published nearly simultaneously with the *Principia* of Descartes.

‡ *Principia*, pars quarta.

§ This idea of a circular motion in connexion with fire seems to have prevailed at a much earlier period.   Thus Seneca says, "Ignis enim natura in verticem surgit, et, si nihil illum prohibit, ascendit." (*Quæst. Natur.* lib. ii. cap. 24.)   *Vide* also Aristotle, Περὶ Οὐρανοῦ, lib. i. cap. 2.

being unhampered by the presence of a large quantity of the third element is present in sufficient quantity to give motion to the globules of the second element associated in large quantity with the substance, but is unable to move the particles of the third element. *Heat* is apparent without light (as in the case of all sensibly hot non-luminous bodies, and to a less extent of all matter), when the *materia cœlestis* has sufficient power to move the particles of the third element, but is so entangled in them that it cannot move the globules of the second element. *Heat and light* are simultaneously produced (as in the case of flame, and in all instances of quick combustion) when, there being many globules of the second element present, the *materia cœlestis* exists in such quantity that it is able to communicate motion both to the second and third elements. The particles of oils, sulphurs, and combustible bodies generally are peculiarly disposed to receive the motion of the *materia cœlestis*; and such bodies are said to be " potentially hot." A nail which is being driven into a block of wood does not grow hot until after it has been driven home by the hammer, because heat is the motion of the insensible parts of matter, not the motion of masses; and as long as the nail itself is capable of moving, the force of the blow is expended in producing that motion of a mass, not in moving the insensible parts of the body. Light consists of globules of the second element agitated by the *materia cœlestis*; there is no transmission of substance, simply of motion. *Lux* is to be distinguished from *lumen*: the former is a propensity to motion, an action which tends to induce motion; the latter is the motion communicated to a medium. Flame tends upwards because it contains a large amount of *materia cœlestis,* which is lighter than air, and which is the cause of lightness in all bodies*.

The physical philosophy of Descartes slightly resembles that both of Epicurus and of Aristotle; it will be observed that the " *materia cœlestis* " in many respects resembles the " αἰθὴρ " of Aristotle; and it is impossible to read the fourth book of the treatise 'Περὶ Οὐρανοῦ' without being forcibly reminded of much similar matter in Descartes's *Principia.* We cannot be surprised that Descartes propounded a dynamic theory of heat, because his system of physical philosophy is essentially of a dynamic character. Happily in the present day we are merging into a dynamic physical system. There have been several laudable attempts to precipitate this end,—among others, the quasi-Cartesian hypothesis of molecular vortices propounded by Rankine, and the dynamic treatment of electrical phenomena proposed by

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* *Principia,* pars quarta. The *Principia* of Descartes was published in the year 1644, consequently in Becher's nineteenth year, and twenty-five years before the publication of the *Physica Subterranea.*

Clerk Maxwell. Already heat and light have been resolved into dynamic phenomena; and it is to be hoped that before long the indefinite term "imponderable fluid" will disappear from our text-books. At a time when we appear to be progressing towards a comprehensive dynamical system, I venture to assert that the *Principia* of Descartes and the '*Whole body of Cartesian Philosophy*' of Anthony le Grand, may be perused by physicists with advantage, especially those portions relating to the inception, continuance, and transference of motion, and the various modes of motion possible to particles of matter. There is indeed some fanciful, and much imaginary matter in the *Principia,* and many relics of a bygone mode of thought; but there is also lucidity, accuracy of expression, and well-sustained reasoning. Let us in perusing it bear in mind that it emanated from an advanced mathematician, an accurate thinker, and one of the most philosophic intellects of all time.

Lemery*, in his famous *Cours de Chimie,* published in 1675 (consequently between the appearance of Becher's *Physica Subterranea* and Stahl's *Zymotechnia Fundamentalis*), seems to have adopted some of the views of Descartes. He asserts that the acid of nitre has a great number of "*corpuscules ignées*" locked up in it, as may be seen by the heating produced when we add it to spirit of wine. "But because," he continues, "there may be some difficulty in conceiving what is meant by little igneous particles (corpuscules ignées), I do understand by them a subtle matter (une matière subtile) which, having been thrown into a very rapid motion, still retains the aptitude of moving with impetuosity, even when it is enclosed in grosser matters; and when it finds some bodies which by their texture or figure are apt to be put into motion, it drives them about so strongly that, their parts rubbing violently against each other, heat is thereby produced." Elsewhere he affirms that the particles of sulphurs are very susceptible of the motion; and he adds, "it seems probable that fire is only a very violent motion of minute bodies round their centre."

Thus far we have observed no attempt to construct a comprehensive theory of combustion. This was first effected by Robert Hooke; and how admirably he succeeded, is, I think, evident from the passages quoted below. The theory was published in 1665, in Hooke's *Micrographia,* in a chapter "On charcoal or burnt vegetables;" and to the fact that it is buried in a mass of irrelevant matter, that it occurs in a work in which one would not expect to find a theory of combustion, and that there is nothing to indicate its position, is probably to be traced the chief cause of its neglect; for in no age has it been well recognized, and

* Born 1645, died 1715.

never sufficiently applauded. The theory is propounded in twelve propositions : the pith of it is given below in Hooke's own words ; and it cannot be better preluded than by his assertion, " This hypothesis I have endeavoured to raise from an infinity of observations and experiments."

"*Firstly,* that the air in which we live, move, and breathe, and which encompasses very many, and cherishes most bodies that it encompasses, that the air is the menstruum of all sulphureous bodies."

"*Secondly,* that this action it performs not until the body be first sufficiently heated."

"*Thirdly,* that this action of dissolution produces or generates a very great heat, and that which we call *fire.*"

"*Fourthly,* that this action is performed with so great a violence, and does so minutely act, and rapidly agitate the smallest parts of the combustible matter, that it produces in the diaphanous medium of the air the action or pulse of *light.*"

"*Fifthly,* that the dissolution of sulphureous bodies is made by a substance inherent and mixed with the air, that is like, if not the very same with that which is fixed in saltpeter, will, I think, readily be demonstrated."

"*Tenthly,* that the dissolving parts of the air are but few . . . . whereas saltpeter is a menstruum, when melted and red hot, that abounds more with those dissolvent particles, and therefore as a small quantity of it will dissolve a great sulphureous body, so will the dissolution be very quick and violent."

" *Twelfthly,* it seems reasonable to think that there is no such thing as an *element of fire* that should attract or draw up the flame, or toward which the flame should endeavour to ascend out of a desire or appetite of uniting with that as its homogeneal and primitive or generating element; but that that shining transient body which we call *flame* is nothing else but a mixture of air and volatile sulphureous parts of dissoluble or combustible bodies, which are acting upon each other whilst they ascend ; that is, flame seems to be a mixture of air, and the combustible volatile parts of any body, which parts the encompassing air does dissolve or work upon."

This theory was adopted by John Mayow[*], who enlarged it by a number of highly ingenious experiments which clearly showed the part which air plays in combustion, together with the compound nature of air.   He further proved that one of the constituents of the air is the supporter of life and combustion, and the cause of putrefaction ; he also assumed it to be the principle of acidity.   These experiments were published many years before Stahl wrote on phlogiston.

[*] Born 1645, died 1676.

Hooke's theory of combustion was published nearly five years before the publication of Becher's *Physica Subterranea* (which laid the foundation of the theory of phlogiston). At this time Stahl was four years old; yet M. Chevreul asserts, " *On doit à Stahl la première explication de la combustion* "*; and still more recently Sir B. Brodie tells us that the theory of phlogiston was the first chemical theory†. While this *idolum specus* remains in the mind of the scientific, I despair of a just recognition of the services of Hooke—of a just appreciation of one of the most sound and comprehensive theories which has appeared in the whole history of scientific thought.

IV. *Of the ideas regarding the calcination of metals which prevailed prior to the rise of the theory of Phlogiston.*

We have finally, before considering the rise of the theory of phlogiston, to glance at the views which prevailed before and during the time of Becher in regard to the calcination of metals.

The process of calcination has always been one of the most important operations in chemistry, and is prominently described in all old chemical treatises. The term *calx*, originally applied to lime, soon came to have a wider meaning, and it was found a convenient term to express anything that was burnt to powder. Geber defines calcination as "the pulverization of a thing by fire by the deprivation of the humidity consolidating the parts"‡; and this broad definition was repeated almost verbatim in chemical works for at least eight centuries after the time of Geber. The ash of wood was its calx; the oxide of a metal was its calx; the ignited residue of a substance dissolved in acid was its calx, as also was the product produced by fusing it with sulphur. Expressed according to the salt, sulphur, and mercury theory, calcination is the expulsion of the combustible and volatile principle of the body calcined, and the resulting ash is its salt or principle of solidity. This last product varied considerably; for while organic matter contains much mercury and sulphur and but little salt, the metals, as a rule, contain much fixed principle, and but little principle of combustibility or of volatility. Such metals as refused calcination by the ordinary means of heating in air were calcined by the addition of nitre or sulphur;

* "Note historique sur les manières diverses dont l'air a été envisagé dans ses relations avec la composition des corps," *Comptes Rendus* for December 12, 1864.

† *Vide* his discourse delivered before the Chemical Society on June 6, 1867, " On the mode of Representation afforded by the Chemical Calculus, as contrasted with the Atomic Theory."

‡ " Est ergo calcinatio, rei per ignem pulverifatio, ex privatione humiditatis partes consolidantis."—*De Alchimia* libri tres.

and it was believed that the added substance helped by its own combustibility to expel the volatile parts of the metal.

Geber observed that lead increases in weight during calcination[*]; and Cardanus added the observation that the gain amounts to one-thirteenth the weight of the lead taken. Now Cardanus, following some of the ancients, supposed everything to possess a certain life, and that life was "*a celestial heat,*" in fact the "subtilis ignis" of other writers. When metals are calcined they *die,* the celestial heat is dissipated, and they become heavier, for the same reason that animals are heavier when dead than when living; for celestial heat tends upwards, and is the cause of lightness[†]. Paracelsus had a somewhat similar idea as regards the separation of the innate heat of the substance submitted to calcination. "By calcination," he writes, "is separated watery moisture, fat, *natural heat,* odour, and whatever else is combustible"[‡]. Cæsalpinus, in a very matter-of-fact way, attributed the increase of weight to soot, which he imagined became mixed with the metal during calcination; others attributed it to the retention of the "vapours of charcoal," or the "volatile salt of charcoal," and some to matter removed from the calcining vessel. In the midst of these diverse opinions there appeared in 1625 the *Praxis Chymiatrica* of Jean Hartmann, containing a chapter by Hamerus Poppius, "De Calcinatione Antimonii per radios solares." When antimony was calcined by converging the rays of the sun upon it by means of a lens, Poppius found that a gain of weight was apparent, just as when it was calcined in a furnace; it was obvious, therefore, that the gain could not arise from the assimilation of soot, or the "vapours of charcoal," or from any of the supposed causes mentioned above. A few years later (in 1629) the matter was investigated by Jean Rey a physician of Bergerac; and the results of his inquiry were published in an essay *Sur la recherche de la cause pour laquelle l'estain, et le plomb augmentent de poids quand on les calcine.* Rey attributed the increase of weight to the absorption of thickened air ("*l'air espessi*"); and the following,

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[*] *Gebiri Philosophi ac Alchemistæ Maximi de Alchemia,* 1531, cap. 35. "Sermo in Saturno."

[†] Nam plumbum cum in cerusam vertitur, ac uritur, tertia decima parte sui ponderis augetur. Hoc fit quia calor cœlestis evanescit: nam certum est adjici nihil, et tamen crescit; cum igitur parratio etiam in animalibus videatur, quæ graviora morte fiunt, quoniam exhalante anima secum calor etiam, ac quicquid ab illo est elaboratum evanescit: manifestum est corpora metallica et lapides ipsos etiam vivere."—Hieronymi Cardani Medici Mediolanensis *De Subtilitate* lib. xxi. (Parisiis, 1551), lib. v. "De Mixtione et Mixtis imperfectis, seu metallicis."

[‡] *De Rerum Natura,* lib. viii.

as I have elsewhere stated*, appears to have been his mode of reasoning :—Air possesses weight ; it may be produced by heating water, which during distillation separates into a heavier and a lighter part ; hence as air approximates to a liquid nature, it may be supposed to be separated into a heavier and a lighter part by the action of heat ; now the heavier part (the " *dregs* ") of air is more nearly allied to a liquid than air, for it has assumed a " viscid grossness;" and this part attaches itself to calces during the process of calcination, and causes such of them as possess much ash to be heavier than before calcination.   If we calcine a vegetable or animal substance, there is no gain of weight, because the assimilated thickened air weighs less than the volatile matter expelled by heat ; but in the case of a metal the assimilated air weighs more than the volatile matter expelled, hence there is gain of weight.   Thus he imagined that all calces, from a vegetable ash to a metallic calx, attract this thickened air.

Glauber some years later suggested that the gain may arise from the coagulation of heat by the metal during calcination. Boyle, in a treatise entitled " Fire and Flame weighed in a Balance," published in 1672, details some experiments which he made in order to determine the amount gained by various metals during calcination.   From the fact that lead and tin were found to undergo partial calcination when fused in sealed vessels, he inferred that " glass is pervious to the ponderous parts of flame," and that the gain of weight is due to the assimilation of " *extinguished flame*," or as he otherwise expresses it, of " *igneous particles*," by the calx.   He further gives it as his opinion that the calx of a metal is not its " terra damnata," but the metal *plus* something assimilated during calcination.   Lemery also maintained that the gain arises from the absorption of " *corpuscules de feu*."

V. *Of Becher and Stahl, and of the rise and development of the theory of Phlogiston.*

Let us now consider the rise of the theory of phlogiston as indicated in the writings of its originator Becher; and while we do so let us keep in view the four relevant phases of prior ideas which I have endeavoured to elucidate in the preceding pages, viz. (α) ideas regarding the " *subtilis ignis*," (β) ideas regarding the three chemical principles, (γ) ideas regarding the process of calcination, and (δ) ideas regarding the nature of fire.

John Joachim Becher was born at Spiers in 1625 : little

* " On the supposed Nature of Air prior to the discovery of Oxygen, Chemical News, vol. x. p. 209.

appears to be known about him ; and the accounts vary considerably. He appears to have been appointed Professor of Medicine in the University of Mayence in 1666, and subsequently Physician to the Elector of Bavaria. In 1680 he went to England and spent two years among the mines of Cornwall and of Scotland ; he died in 1682.

The works of Becher which most concern us are the following :—

Physica Subterranea, published in 1669.

Supplementum Primum in Physicam Subterraneam, 1671.

Supplementum Secundum in Physicam Subterraneam, 1675.

Minera Arenaria Perpetua, sive Supplementum Tertium in Physicam Subterraneam, 1680.

The dedication of this last work is dated from London, and is sufficient answer to those who affirm that Becher never went to England.

The writings of Becher are most barbarous in style ; but it is just to add that he apologizes for this, ending his apology with the sentence, " *sic rebus attentus, verba neglexi,*" which is fully justified. The style and diction are not alone deficient, for the matter itself is most obscure and unintelligible ; there is great want of definiteness of expression, and some passages appear to actually contradict others : a notable example of this is to be found in the accounts which are given of the nature of mercury (α) in the *Physica Subterranea,* (β) in the *Concordantia Chymica,* and (γ) in the *Supplementum Secundum.* I cannot promise to faithfully interpret the ideas of Becher (for Stahl himself, living at the same period, and recognizing Becher as his master, sometimes expresses doubts as to the precise meaning of certain passages) ; but I have endeavoured as far as possible to separate the intelligible from the occult portion of his writings; and after so doing there does appear a very sensible consistency in regard to the greater number of major points.

Becher considered water and earth to be the primal elements, and he divided the latter into three kinds—(α) *Vitrifiable earth,* (β) *inflammable earth,* and (γ) *mercurial earth.* These have been regarded as specifically different from, and incapable of being compared with, the elements of any previous physical system ; but I cannot fail to recognize in them, under other names, the three chemical principles *sal, sulphur, mercurius* ; and this being admitted, the system of Becher is *à priori* assimilable with the four-element system. Let us then assimilate Becher's theory with the three-element theory of the chemists, and regard the " vitrifiable earth " as salt (the principle of fixity and solidity), the " inflammable earth " as sulphur (the principle of combustibility), and the " mercurial earth " as mercury (the principle of volatility).

Becher sometimes designates the three earths as " gradus sulphuris " *,—the first " fixed sulphur," the second " volatile sulphur," the third " combustible sulphur ; " this last he speaks of indiscriminately as "*sulphur adustibile,*" "*sulphur ardens,*" or "*sulphur* φλογιστὸν," the last word being simply the Greek representative of *ardens* †. The latter word is most used ; indeed I do not think the word φλογιστὸν occurs once in the *Physica Subterranea,* and certainly not half a dozen times in the *Supplementum Primum* and *Supplementum Secundum.*   Becher regarded the combustible principle as an innate heat.   " Sulphur est metallorum calidum innatum," he writes in the *Supplementum Secundum* ; and, again, argentum vivum is pervaded " spiritu quodam sulphureo, archæo minerali, igne interno, seu, ut Basilius loquitur, primo mobili metallorum."   When argentum vivum is fixed by an acid, or otherwise, it loses this innate heat, and its particles become motionless.

Becher built up various substances from his elements in a somewhat arbitrary fashion ; in tracing a few of these it will be convenient to designate the elements by letters.

Let *water* be represented by W.

The vitrifiable earth, or principle of solidity, by S.

The inflammable earth, or principle of combustibility, by C.

The mercurial earth, or principle of volatility, by V.

Then the following expressions will represent the composition of a few well-known substances according to Becher :—

$W + S =$ the " universal acid."

$W + C =$ oils.

$(W + S) + C =$ bitumen.

$\{ (W + S) + C \} + (W + S) =$ sulphur.

$(W + S) + C =$ saltpetre.

$(S + C + V) + (S + V) =$ arsenic.

$(S + C + V) + V =$ argentum vivum.

$\{ (S + C + V) + V \} + \{ [(W + S) + C] + (W + S) \} =$ cinnabar.

The meaning of the above will be readily intelligible : thus water *plus* the inflammable earth in various proportions constitute different kinds of oils ; bitumen *plus* the " universal acid " constitute sulphur, and so on.   It is, however, to be borne in mind that Becher has nowhere represented the composition of bodies by the above means (which is employed for the sake of

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* *Supplementum Secundum.*

† Φλογιστὸς is an adjective derived from φλογίζω, *to inflame*, which is related to φλέγω, *to burn*, and to φλὸξ, *flame.*   The word φλογιστὸς is rarely used by ancient writers, and hence is not often met with in our lexicons.   In the very extensive *Lexicon Græco-Latinum* of Robert Constantinus, published in 1592, the word is given with only two meanings, thus :— φλογιστὸς—*ardens, splendidus.*

simplicity and intelligibility) ; but he has stated in writing that such is the composition of the bodies specified ; we do not know by what means he arrived at such conclusions.   I may allude *en passant* to the very apparent inception of the idea of chemical affinity in the writings of Becher.   One substance "*attrahet* " another, in virtue of its "*affinitas*;" "*reactio*" ensues ; he pertinently remarks that the stronger the "subjecta reagentia, hoc fortior etiam est reactio, et reactionis effectus."

The term *phlogiston* appears to have been solely used by Becher in the sense mentioned above, viz. as an adjective; he did not use it as a substantive, he did not designate the matter or principle of fire by it; indeed he remarks in the *Physica Subterranea* that *materia ignis* is well called "*salamandra*," because it feeds upon fire.   Moreover Stahl in the *Specimen Becherianum* writes, "Materia et principium ignis, non ipse ignis, *ego* Phlogiston appellare cœpi;" and it is curious, as indicating the transition, that in his earlier works the word is used as an adjective : thus in the *Zymotechnia Fundamentalis*," published in 1697, I find the word "φλογίστατον."

Becher diligently consulted the works of former and contemporary chemists ; I do not remember to have met with any previous writer who so constantly quotes the opinions of others, and who so persistently endeavours to support his own opinions by those of his predecessors.   He was thoroughly versed in chemical literature ; if this had not been the case, he could not have commenced that plan of systematization which was so extensively carried out by Stahl.   As the facts of a science accumulate, generalization becomes a necessity ; and this is usually effected by means of a theory.   In the time of Becher a vast number of chemical facts were known, but they were the disconnected links of a chain, and were loosely scattered about ; Becher laudably attempted to introduce order among them.   He did not accomplish this ; but the more comprehensive (and less original) mind of his disciple Stahl, taking his design as the starting-point, did accomplish it.

Stahl converted Becher's φλογιστὸν into a substantive, and applied it to designate the *materia ignis* so often spoken of in the works of former writers on chemistry ; and at the same time he endued it with certain extended functions, many borrowed from Descartes, some added by himself.

George Ernest Stahl was born at Anspach, in 1660.   He pursued his studies in the University of Jena, and made such progress in medicine that in 1694 he was appointed second Professor of Medicine in the recently founded University of Halle, which appointment he held for twenty-two years.   In 1716 he was appointed physician to the King of Prussia, and he then re-

signed his professorship and went to reside in Berlin, where he died in 1734. Stahl was eminent as the expounder of new views both in medicine and in chemistry ; and it is difficult to say in which science he was considered most to excel by his contemporaries. He was a very voluminous writer ; the principal works in which he developes the theory of phlogiston are the following :—

Zymotechnia Fundamentalis, published in 1697.
Specimen Becherianum*, published in 1703.
Fundamenta Chemiæ, published in 1723.
Experimenta CCC numero, published in 1731.

In the *Zymotechnia* Stahl has roughly sketched out the theory of phlogiston ; in the *Specimen Becherianum* he has elaborately annotated passages from Becher's *Physica Subterranea,* and has to a great extent blended the views therein contained with his own. The *Fundamenta Chemiæ* is a text-book of phlogistic chemistry, while in the *Experimenta CCC numero* we have a number of experiments in support of the theory, and answers to supposed objections. The diction throughout is most barbarous, the Latinity utterly unpolished ; and in the third part of the *Fundamenta Chemiæ* Stahl not unfrequently introduces both German and Latin sentences into the same paragraph. The following passage is from the *Fundamenta Chemiæ* :—

" Sonst ist, wie gesaght, das principium φλογιστον im phosphoro, und muss daraus noch die kunst erfunden werden, mixtiones oleosas pingues, seu mixtiones pinguedinum, per artem zu machen, als oleum weil in ihm das φλογιστον purius zu finden." It was this habit, exercised in a milder form, which caused Becher to speak of his combustible principle as *sulphur ardens* and *sulphur* φλογιστον indiscriminately.

Stahl followed the ancients in believing in the existence of two kinds of fire—(*α*) ordinary visible fire, requiring combustible matter and air for its nutriment, which he calls *ignis* or *flamma,* and (*β*) the invisible fire (*materia ignis* or *phlogiston*), which becomes *ipse ignis* when associated with particles which readily assimilate its motion.

The *materia ignis* he conceived to be a very subtle matter, capable of penetrating the most dense substances; it neither burns, nor glows, nor is visible †; it is agitated by an igneous

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* Stahl was excessively verbose in the titles of his works, as elsewhere ; the following may serve as an example :—" Specimen Becherianum sistens fundamenta, documenta, experimenta, quibus principia mixtiones subterraneæ et instrumenta naturalia atque artificialia demonstrantur. Ex autoris scriptis, colligendo, corrigendo, connectendo, supplendo concinnatum exhibit Georg. Ernestus Stahl, Prof. Publ. Hall. et Acad. Nat. Cur. Colleg."

† *Vide Exp. CCC numero,* No. 38.

motion ("igneo motu"), and it is capable of communicating
that motion to material particles apt to receive it. The particles,
when endued with this rapid motion, constitute visible fire. Thus
it will be perceived that precisely the same kind of distinction as
that which Descartes admitted to exist between *lux* and *lumen*
was by Stahl assumed to prevail between *phlogiston* and *ignis*
(see p. 15). The igneous motion is "gyratorius seu verticillaris."
Fire is an aggregate of a great number of particles readily moved
by the igneous motion, and in very vehement motion ; the mo-
tion is circular and not progressive : "Igneus motus in seipso
est verticillaris, immanens in loco, non progressivus" (Exp. 81) ;
and again he defines it as "Verticillaris seu circa centrum
materialium corpusculorum" (Exp. 143)*. Fire throws out
different particles, varying with the nature of the substance
which feeds it ; thus the flame of sulphur corrodes metals, while
that of charcoal does not affect them. Heat is an intestine
motion of the particles of matter. We must specially distin-
guish between the *materia* and the *forma* of fire, Stahl tells us :
the former is the thin all-pervading medium composed of very
moveable particles, in fact phlogiston ; the latter is the motion
itself. The *materia* is passive, and apt to receive the motion ; the
forma is active, and conveys the motion. In fluids each particle
is in a state of rapid motion ; and this is essential to fluidity.
Solution by a fluid only takes place when the particles of the
body to be dissolved possess less motion than those of the sol-
vent ; moreover the particles of the body to be dissolved must
be of two kinds, some more capable of receiving motion from
the particles of the solvent than others. It thus happens that
an inequality of motion is communicated to the particles of the
compound ; that is to say, some are caused to move with greater
velocity than others, and solution of continuity necessarily en-
sues. The solutive action is necessarily hastened by heat, because
the particles of the solvent are caused to move more quickly,
and consequently sooner affect the particles of the body to be
dissolved.

The general application of the doctrine of phlogiston to the
explanation of chemical phenomena is too well known for it to
be necessary for me to enlarge upon it here. I may briefly state,
however, that as a rule the expression "*loss of phlogiston*"
means, in the language of modern chemistry, *combination with
oxygen*; and conversely, "*gain of phlogiston*," or "*assimilation
of phlogiston*," signifies deoxidation. For instance, lead during
calcination loses phlogiston ; for lead, according to the phlogis-
tians, is calx of lead *plus* phlogiston, and when the calx is heated

* Compare the matter of this and the preceding page with that of pages
14 & 15.

with substances rich in phlogiston, the latter is reabsorbed, and the metal is the result.   Sulphur is composed of sulphuric acid *plus* phlogiston ; therefore sulphur *minus* phlogiston is sulphuric acid.   Phlogiston is spoken of as possessing " predisposing affinity " for substances.   We perceive, by reference to the ideas of Becher regarding the constitution of bodies, that he considered sulphur a compound of the combustible principle with the "universal acid," the principle of acidity.   Stahl adopted the idea of the " universal acid ; " and some of the later phlogistians regarded sulphuric acid in that light.

Shortly before Lavoisier, by an admirable series of experiments, proved the fallacy of the theory, the principal properties of hydrogen were made known, and in this gas the phlogistians took refuge as a last resource.   Hydrogen, they said, is phlogiston ; when certain metals are dissolved in acid it visibly escapes ; and when the calces of these metals are heated in hydrogen, they become metals again by absorbing the gas.   The analogy with hydrogen appeared complete in some respects ; but the properties conferred upon the supposed phlogiston of Stahl were utterly different from those of hydrogen in many respects. The perversion of the original theory did not, however, end with the attempt to prove the identity of hydrogen with phlogiston ; for after the abandonment of the theory in France it still found supporters in Germany ; and some of the more ardent (among them Gren) preferred to grossly garble the theory rather than relinquish it. When, however, in 1792 the Academy of Sciences of Berlin abandoned the theory and adopted the views of Lavoisier, the controversy which for some years had raged between the phlogistians and the antiphlogistians was virtually at an end, although a few of the former carried their views into this century.

.VI. *Of the syncretistic nature of the theory of Phlogiston.*

Having traced the development of the phlogistic theory, let us now consider its nature and influence.

Phlogiston was a new name for an old principle.   We have seen that the idea of the existence of a subtle fire innate in matter has pervaded physical philosophy from the earliest times. *Phlogiston* was another name for the "*pure fire*" of Zoroaster, the " ἀτεκνε-κον πῦρ " of Zeno, the "*subtilis ignis*" of Lucretius, the " *elemental fire*," "*astral fire*," "*sulphur*," or "*sulphureous principle*" of the Chemists, the "*calor cœlestis*" of Cardanus, the "*sideric sulphur*" of Paracelsus, the "*materia cœlestis*" of Descartes, the "*terra inflammabilis*" of Becher.   The functions of this entity had been varied by different thinkers almost as much as its name, until Descartes gave them accurate definition.   The

theory of phlogiston was the theory of the "materia cœlestis" extended in a chemical direction. Phlogistic chemistry was Cartesian chemistry. Descartes defined the physical functions of the *materia cœlestis*; Becher and Stahl defined its chemical functions, and applied them to the explanation of diverse chemical phenomena. Throughout the writings of Becher and Stahl there is a sprinkling of Cartesianism; they did not, however, adopt the system in its entirety, but they appear to have discarded the second and third elements, and adopted the first as the parent of their own system. Enough, I think, has been said in the preceding section to show clearly that the dominant functions of the *materia cœlestis* were conferred upon its synonym phlogiston.

The principal operations of old chemistry were performed by fire; hence *pyrotechnia* ($\pi\hat{\upsilon}\rho$ $\tau\acute{\epsilon}\chi\nu\eta$) was one of the many names by which the science was once known; "car en effet," says Lemery, "c'est par le moyen du feu qu'on vient à bout de presque toutes les opérations chymiques"*. Old chemical treatises usually begin with the definition of various operations; and prominent among these we find *calcinatio, ignitio, cinefactio, reverberatio, desiccatio, sublimatio,* and *distillatio,*—all operations of fire. The only process of chemical analysis (a term which we frequently find in seventeenth-century works) was effected by fire. A rude fractional distillation of such bodies as could be distilled was called their *analysis,* the different stages of the process being indicated by the various modes of heating applied: thus the first would be a water-bath; secondly, an oil-bath; thirdly, a bath of sand or iron-filings heated below redness; fourthly, a dull red heat; fifthly, a bright red heat; and if there was any residuum in the retort it was heated in a wind-furnace. The product of each process was collected separately, and the last residuum was called the "*caput mortuum,*" or "*terra damnata.*" Thus wax analyzed by the above process was said to be composed of "a phlegm," "a spirit," "a butter," and "a caput mortuum." Such bodies as yielded no product on distillation were analyzed by being calcined, either alone or with nitre or sulphur, or by dissolution in an acid, evaporation to dryness, and ignition. The term *analysis* was used in its broadest and most literal sense; immediately that a substance was split up into two or more parts it was considered to be analyzed. Now, as in all known instances fire appeared to act by splitting up and dissociating bodies, and expelling their more volatile parts, the calcination of a metal came to be considered the expulsion of its more volatile parts, and the calx was called its "caput mortuum." So also sulphur and phosphorus when burning were believed to lose their more vola-

* *Cours de Chimie,* p. 2.

tile parts. Boyle had suggested that, in these operations of fire, the substance acted upon is modified and altered by the fire itself, and that the product of distillation or calcination does not exist as such in the substance distilled or calcined; he had further suggested that calcination was due to the absorption of " *igneous particles.*" Descartes had for the first time recognized and defined the action of a rapidly moving æthereal medium in effecting changes in matter, and had made *fire* a product of its action. The experiments of Rey and of Mayow, and Hooke's theory of combustion were forgotten or misunderstood, or were considered unassimilable with chemical phenomena in general. Putting all these facts together, the nature of the process of evolution which terminated in the theory of phlogiston has, I trust, been intelligibly demonstrated.

The theory of phlogiston was essentially and completely a syncretistic theory. It was built up of *idola theatri** collected from various sources; and these were cemented together by the particular *idola specus*† of Becher and Stahl. In this process of syncretism the merit of these men lay; their fault was a too hasty generalization. In that stage of chemistry syncretism was inevitable; indeed all theories are more or less tinctured by it, with the exception of those which emanate from a new mode of experimenting, such, for example, as Kirchhoff's theory of the constitution of the sun. But take any theory unsupported by direct experiment (our own atomic theory for instance), and observe how perfectly syncretistic it has been in every stage of its development. Originating at a very early period in India, and there receiving extensive development at the hands of Kanáda, the atomic theory passed into Greece, and was adopted and extended by Leucippus, Democritus, and Epicurus; later it found supporters among the Romans; and it frequently crops up from the rugged surface of mediæval philosophy as some one of the greater thinkers of the period made it the basis of, or gave it prominence in, his physical system. Descartes thoroughly adopted it, and extended some of the ancient dogmas until the most diverse phenomena were explained by it; and thus it endured, often adopted, and as often modified, until, as the last process of the syncretism, Dalton applied it to chemistry. Thus step by step we cross great eras in the development of thought;

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* " Sunt denique idola quæ immigrarunt in animos hominum ex diversis dogmatibus philosophiarum, ac etiam ex perversis legibus demonstrationum; quæ *idola theatri* nominamus."—*Novum Organum*, lib. i. aph. 44.

† " *Idola specus* sunt idola hominis individui. Habet enim unusquisque (præter aberrationes naturæ humanæ in genere) specum sive cavernam quandam individuam, quæ lumen naturæ frangit et corrumpit."—*Novum Organum*, lib. i. aph. 42.

there is no sudden and gigantic stride; a theory proceeds by slow evolution until it dominates or is destroyed. It was thus with the theory of phlogiston: arising under the most favourable conditions it attained full development, became most cardinal, most sovereign, and fell. For twenty-eight years it was looming a half-formed thing through the mists of chemistry; for thirty-four years it was growing in strength and proclaiming its dynasty; for fifty-four years it was dominant, and it was fully ten years yielding up the ghost. There are men amongst us now who have listened to the echoes of its departing steps.

Becher and Stahl were the prophets of a new mode of chemical thought, essentially classificatory, systematic, and syncretistic. In their day chemistry was at the commencement of a period of transition, and they bridged the gap which existed between empirical chemistry and modern chemistry. They did not collect the materials for the structure, they did not altogether construct it, but they designed it, and helped in the work of building. Albeit a bad bridge, and built upon shifting sands, yet it was a channel of escape from mystic science, and many passed over to take refuge on the other side.

The theory of phlogiston was highly ingenious, and it was elaborated with great assiduity and perseverance, but it was not founded upon direct experimental deductions; indeed this could not be the case, on account of the subtlety of the supposed entity, and the consequent impossibility of experimenting with it. Phlogiston was believed to be something like that subtle medium which has for ages been known by its present name, *the æther*; indeed phlogiston is sometimes called *"materia ignea ætherea"**. It had never been seen; its real nature and properties were entirely unknown; for it had never been separated in the free state: all was conjecture; yet it was agreed to refer certain phenomena of chemical change to its absorption or rejection by the mutating substance. Macquer says we cannot tell how phlogiston is fixed by substances, and adds, very unphilosophically, "without pretending to guess the cause of the phenomenon, let us rest contented with the certainty of the fact, the knowledge of which will undoubtedly procure us considerable advantages." (We cannot but think that this "resting content" with the theory did much to retard chemistry during the phlogistic period.) The phlogistians were most assiduous in collecting *"Instantiæ convenientes in naturâ calidi,"* but they were slow to apply *"rejectio naturarum a formâ calidi"†*. The generalization was too hasty and was insufficiently supported by

* Vide *Conspectus Chemiæ Theoretico-practicæ e dogmatibus Becheri et Stahlii.* Auctore D. Joanne Junckero. 1744.
† *Novum Organum,* lib. ii. aphs. 11 & 18.

facts.   One of the fundamental propositions of the theory was that the calcination of a metal is the expulsion of its phlogiston, and that the calx can only be reduced in the presence of a body which can communicate to it the lost phlogiston.   Yet it was well known that mercury becomes a calx when heated to a certain temperature, and that the calx is revived by increasing the temperature.   But the phlogistians generally omitted the explanation of this from their handbooks.   Becher states that the calx is formed by the absorption of a " certain mercurial sulphur," viz. a certain volatile combustible body.   Stahl states that the calx of mercury does not weigh more than the mercury which produced it; yet before he was born Boyle had employed balances which turned with one thirty-second of a grain for chemical operations.   That thorough and ardent phlogistian Macquer sacrificed the fact to the theory; he would not allow that red oxide of mercury was a calx, consequently he heads the section which gives an account of its preparation as follows :— " Donner au mercure par l'action du feu *l'apparence* d'une chaux métallique "*.   The fact that it can be reduced to the metallic form without the presence of a body containing phlogiston proves, he asserts, " that during that long calcination† it lost none of its phlogiston."   Another objection to the theory was the fact that calces weigh more than the metals which produce them, or, otherwise stated, that the loss of phlogiston is synonymous with gain of weight; but this received an explanation which was somewhat plausible at first sight.   Ancient writers frequently assert that all fire and heat have a tendency upwards ‡; some attributed this to the attraction of the pure fire above.   According to Descartes, flame is pointed and tends upwards because it contains a good deal of *materia cœlestis*, which is much lighter than air, and confers lightness upon bodies.   So also said the phlogistians :—phlogiston confers negative weight; it is a principle of levity, and when associated with matter it lessens its weight, just as inflated bladders lessen the weight of a swimmer.   It will be remembered also that Cardanus gave a very similar explanation of the increase of weight of calces more than a century before the birth of Stahl (*vide* p. 19).   Macquer, after remarking that 100 lbs. of lead produce 110 lbs. of minium, frankly owns that not one of the many hypotheses proposed to account for the gain of weight during the process of calcination is satisfactory.

* *Vide* his *Elémens de Chimie-pratique*, 1751.

† " Mercurius precipitatus per se," as it was called, was prepared by gently heating mercury in matrasses with long necks for a length of time, generally for about three months, but sometimes for as many as fifteen.

‡ Thus Aristotle, " ἐπεὶ κατὰ φύσιν γε τὸ θερμὸν ἄνω πέφυκε φέρεσθαι πᾶν."—Μετεωρολογικῶν lib. i. cap. 4.

The phlogistic theory is always associated with the name of Stahl; but it may be well for us to inquire with what reason. The principle itself had been recognized from the earliest ages; its functions had been developed physically by Descartes, and to some extent chemically by Becher; the name was borrowed from Becher. Stahl converted Becher's term into a substantive, and conferred it upon Descartes's first element; he also extended the attributes of the principle, applied it diffusively, and brought the full force of his comprehensive and methodical mind to bear upon the subject. In the present day we give too much credit to Stahl, or at least too little to Becher. It was not the wish of Stahl that the theory should be attributed to him alone; for he actually developed it in the form of notes to portions of Becher's *Physica Subterranea,* a treatise which he designates " *opus sine pari.*" Stahl did not consider that Becher's genius was sufficiently recognized by the world[*], and he never wearies of praising him. At the end of a laudatory chapter in the *Specimen Becherianum* he exclaims in his turgid and somewhat crass phraseology, " *Audite hoc, manes Becheriani. Dixi.*"

Of the influence of the theory of phlogiston I need say but little. It was not the first chemical theory; it did not give the first explanation of combustion; and it was established in the face of facts which carried with them its refutation. When the first stage of its development was passed facts were adapted to the theory, and phenomena were tortured and garbled so as to fit in with it, by which means the progress of chemical science was somewhat retarded. Even when Lavoisier had conclusively proved the fallacy of the theory, this blind adherence shut the eyes of the phlogistians to the merits of the new system, and to the utter falsity of their own. Nevertheless the theory exercised influence for good; for by its means a certain amount of order was introduced among a vast chaotic mass of chemical facts, and phenomena were classed together and reasoned upon together, and together submitted to similar processes of mental analysis after the manner so strongly advocated by Francis Bacon.

When Mdme. Lavoisier, habited as a Greek priestess, burnt the writings of Stahl upon an altar dedicated to the new science, the downfall of the theory of phlogiston was not alone typified; for in that holocaust perished the vast system of empiricism which had pervaded chemistry from the time of its origin until

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[*] Juncker, in the *Conspectus Chemiæ,* speaks of Becher in the following terms :—" Vir magno ingenio atque judicio, inque omni ferme scientiarum genere versatus, imprimis etiam chemiæ studio addictus, quo felicissime usus est ad illustrandam physicam, et vera rerum principia ac mixtionem corporum investiganda atque edocenda."

then—relics of Egyptian and Chaldæan lore, of an age of fana-
ticism, of intellect perverted by a false enthusiasm.   Phlogistic
chemistry had arisen on the ruins of the older structure of me-
diæval chemistry ; and from it arose modern chemistry.   Let us
be fain to remember that the mother died in giving birth to the
child.   The new science was as Dionysius born of the dying
Semele ; and while we worship the son, like the ancients we
have not forgotten to raise a statue to the mother.

14 Denbigh Place, S.W.,
    December 12, 1867.

II. *Contributions to the Mineralogy of Nova Scotia.   By* Professor
    How, *D.C.L., University of King's College, Windsor, Nova
    Scotia.*
            [Continued from vol. xxxiii. p. 340.]

III. *Borates and other Minerals in Anhydrite and Gypsum.*

SILICOBOROCALCITE, *a New Mineral.*—In former papers
        I have pointed out the existence of two distinct borates in
the gypsum of this vicinity, viz. natroborocalcite* and crypto-
morphite†, both hydrated borates of calcium and sodium—the
latter exclusively, the former occasionally, associated with glauber
salt—and have adverted to the possibility of their being some-
times found together in intimate connexion with the latter‡.
The very large quantity of quarried " plaster " (as both anhydrite
and gypsum are called here) to be seen at Windsor, not less than
104,000 tons having been cleared in twenty-one months from
this port, of which the greater part has been shipped from its
own wharves, affords abundant material for the study of its va-
rieties and the minerals they contain.   A short time ago I ob-
served natroborocalcite in plaster from two quarries distant from
its original locality and from each other, but in the same district,
as will be described further on,—and also a mineral, evidently
different, which proved to be an addition to the short list of
natural borates, and to the still shorter list of silicated borates.
The mineral exhibits very different degrees of hardness ; the
hardest specimens are found in anhydrite, the softest in gypsum,
both matrices occurring in the same deposit.   The hard mineral
is in white, rounded, often egg-shaped nodules, brittle, and of
nearly even and smooth fracture, which is well shown in the
broken masses giving almost flat surfaces continuous with those

* Silliman's Journal, September 1857 ; and Edinb. New Phil. Journ.
July 1857.
† *Loc. cit.* 1861.   ‡ Chemical News, 1867.

of the anhydrite in which they are imbedded; these surfaces
are dull. The nodules are generally about the size of filberts or
pigeons' eggs, but occasionally larger; the largest specimen I
have is a fragment about 2 inches in diameter: they sometimes
show, when detached, a subvitreous lustre on the exterior. The
mineral is translucent in thin fragments; under the microscope
its powder is seen to be perfectly transparent and crystalline;
the form, to judge from the cleavage, is possibly rhombic. The
greatest hardness is about 3·5; specific gravity 2·55. Before
the blowpipe, the hardest fragments decrepitate strongly, and all
fuse readily to a clear colourless bead, making the inner flame
green, deep green when the mineral has lain some time in water.
Fragments fuse even in the flame of a lamp to a colourless
blebby glass, which, when further heated before the blowpipe,
froths considerably, and finally becomes quite clear. The trans-
parent bead can be rendered opake by sudden insertion in, and
removal from, the oxidizing flame, probably from the formation
of bubbles of boracic acid which cannot escape till the mass gets
further heated; for on re-fusion the bead becomes clear again,
and remains so on prolonged heating. These reactions distin-
guish the mineral from natroborocalcite, which colours the flame
yellow at first, and fuses readily to a clear colourless bead, which
can also be rendered opake by the method just given, but which
on prolonged fusion becomes so reduced in bulk as to leave the
wire-loop nearly empty; the flame meanwhile becomes decidedly
greenish yellow. In the former case the presence of silica is no
doubt the cause of the permanent transparency. A minute
quantity of either mineral with a drop of dilute hydrochloric
acid gives the boracic-acid test with turmeric paper most readily.
The new mineral before ignition gelatinizes perfectly in two or
three minutes when its powder is stirred with cold hydrochloric
acid,—after ignition also, when left in contact merely for some
time. In a closed tube it decrepitates and gives much water.
In the following analyses the results under I. were from a nodule
in anhydrite; those under II. from several fragments, some of
which were perfectly dull and opake, while others were lustrous
in parts of the exterior. The absence of soda was proved by
testing after removal of boracic and silicic acids by heating with
fluor and sulphuric acid; the boracic acid was estimated by
deficiency after gravimetrical determination of the other consti-
tuents in the regular way. Analysis of the air-dried hard mineral
gave :—

	I.			II.
			Mean.	
Water . . .	11·51	11·60	11·55	11·62
Lime	28·90	. . . .	28·90	28·04
Sulphuric acid .	. . . .	1·03	1·03	0·80
Magnesia . .	. . . .	trace	trace	
Silica	15·12	15·27	15·19	15·44
Boracic acid .	. . . .	. . . .	43·33	44·10
			100·00	100·00

The softest mineral, found in nodules imbedded in gypsum, is so unlike the preceding in hardness that at first I thought it might be effloresced glauber-salt which I had formerly met with in a similar matrix (see papers above referred to). It is like soft chalk or coherent flour, so that it is very difficult to separate pieces of the rock holding it without losing a great deal under the blows of the hammer. Its flame and blowpipe-reactions, except that it does not decrepitate, are those of the harder mineral; it colours turmeric and gelatinizes with equal ease. Analysis of a specimen like flour, obtained by myself among débris at the quarry, gave (air-dried):—

	III.
Water	12·20
Lime	28·85
Sulphuric acid	1·86
Magnesia	trace
Silica	14·64
Boracic acid	42·45
	100·00

These results agree so closely with the foregoing from different specimens in a distinct matrix, that there can be no doubt they all relate to a different mineral whose composition is constant in its varying physical conditions. The percentages correspond remarkably well with those calculated from the formula to which they lead. The results placed below as found are those of III., the analysis just given, after deduction of the quantity of gypsum equal to the sulphuric acid obtained, which is much greater in this than in the preceding analyses, whose numbers are so obviously similar that deduction in all is quite superfluous :—

|	Calculated.		Found.
$5\,HO$ =	45	11·43	11·84
$4\,CaO$ =	112	28·44	28·69
$2\,SiO^2$ =	61·62	15·65	15·25
$5\,BO^3$ =	175·20	44·48	44·22
	393·82	100·00	100·00

Of the various modes in which the constituents of the mineral may be arranged, I prefer the following, and therefore, using the notation employed in mineralogy, propose the formula

$$2\,CaO\,SiO^2 + 2\,(CaO\,2\,BO^3,\,HO) + BO^3,\,3\,HO$$

as that of the new mineral to which I give the name silicoboro-calcite, chosen as companion to that of natroborocalcite, the essential chemical difference between minerals found in the same region, and even, as will presently appear, in the same matrix, occasionally being clearly indicated by these appellations: the formula of the latter, according to my own results, when re-written so as to include some grouping seen above, is

$$NaO\,2\,BO^3,\,10\,HO + 2\,(CaO\,BO^3,\,HO) + BO^3,\,3\,HO.$$

For comparison's sake, I add the formula of cryptomorphite (the other borate found in gypsum here), also rewritten,

$$NaO\,2\,BO^3,\,6\,HO + 3\,(CaO\,2\,BO^3,\,HO) + BO^3,\,3\,HO,$$
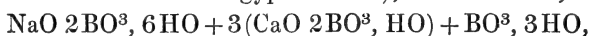
so that relations can be traced between these geologically allied minerals.

The constituents of silicoborocalcite are those of datholite, the only other known hydrated silicated borate of calcium, for which Berzelius gave the formula

$$CaO\,BO^3 + CaO\,2\,SiO^2 + HO,$$

an expression exhibiting proportions very unlike those shown above to exist in the new mineral. In datholite, as in all silicated borates, the boracic acid is sometimes held to be basic[*]. On this view, excluding water,

In datholite the ratio of O in SiO^2 to that in the bases is $4:5$
In silicoborocalcite „ „ „ $4:19$

The ratio of the same to that in all the constituents is in the former $2:3$, in the latter $2:12$; the relations thus brought out in silicoborocalcite are so unlike those in any known compound, that silica cannot be the only acid present. The formula I have proposed contains two of Wollastonite, two of normal hydrated biborate of calcium, and one of Sassolin. While datholite and silicoborocalcite are quantitatively unlike and physically different on comparing the ordinary crystallized specimens of the former with the nodules of the latter above described, there is a remarkable resemblance between these and the exceptional state in which Whitney found datholite in a greenish magnesian silicate near Lake Superior. I refer to the perfectly white and opake nodules looking like the finest marble, or some kinds of Wedgewood

[*] Dana's ‘Mineralogy,’ 4th edit., vol. i. p. 207, and vol. ii. p. 335.

ware*. In the case of silicoborocalcite the crystals may be found, although it is best known in nodules; indeed, as will be mentioned immediately, it does sometimes appear crystalline. I carefully examined a specimen of anhydrite and one of gypsum, not earthy, holding the mineral, and detected in both a very small amount of silica, perhaps some two- or three-tenths per cent.

The small quantity of sulphuric acid recorded in the foregoing analyses arises from the presence of a little selenite, which is very frequently most intimately associated with the new mineral. In the hard form in anhydrite thin bands of selenite are often seen running through the nodules, which sometimes split so as to leave a plate of it on the exposed surface. In gypsum the nodules are sometimes distinctly banded with alternations of the two minerals, and are often quite cellular, walls of selenite standing up between cavities retaining more or less borate. The selenite sometimes carries Arragonite; and this or calcite is occasionally observed on the surface of the anhydritic matrix. Natroborocalcite occurs rather abundantly in an earthy gypsum holding the soft silicated borate, the minerals being independent nodules; and very well-marked coralloidal Arragonite or flos ferri is occasionally found in cavities along with the borate in gypsum: this newly observed fact is interesting, as it was in gypsum of Arragon that Arragonite was first found†. The locality to which the preceding description refers is Brookville, a property about three miles south of the Clifton quarry, close to Windsor, where natroborocalcite was first observed. Brookville is on the southern edge of the deposits of plaster in this neighbourhood, and Clifton on the northern; the deposits extend east for more than forty miles; and I have found silicoborocalcite in a pure-looking gypsum from a quarry on their range at Newport, about six miles to the east of Windsor. Here it does not seem to be so abundant as at Brookville; and it differs somewhat in external character, since it is in white flattened nodules of a *glistening crystalline* appearance, easily separable with a knife into rather gritty particles: it is closely associated with selenite. I identified it by the blowpipe-reactions and by qualitative analysis; the powder stirred with cold hydrochloric acid gelatinized perfectly.

*New localities of Natroborocalcite.*—Both Brookville and Newport are new localities for this mineral, which has been mentioned as occurring at the former in the soft blue earthy gypseous matrix of the silicated borate; it is much the more abundant of the two. It is in its characteristic nodules sometimes

* Supplements to Dana's 'Mineralogy,' Silliman's Journal, May 1860 and May 1861.
† Nicol's 'Mineralogy,' p. 296.

as large as a hen's egg, generally consisting of silky white fibrous crystals; these form with the dull blue matrix fine cabinet specimens.   It is found also in common white gypsum, in selenite, and in fibrous gypsum ; sometimes it has on its surface crystals of calcite or Arragonite.   At Newport it appears to be much less abundant than at Brookville, and to occur in white gypsum only. At both these places the mineral is imbedded in the matrix in solitary nodules; in one case I observed a nodule in a cavity whose base was lined with crystals of selenite, among which it was implanted.   The nodules lately found, especially at Newport, are not always visibly crystalline, and are generally, even when silky fibrous, much harder in the interior than on the outside, the difference being about as 3 to 1.   Careful analysis, however, shows them to contain water, lime, boracic acid, and soda, the latter being unmistakeably found in essential quantity after removal of boracic and silicic acids by heating with fluor and sulphuric acid : the crystalline form was seen under the microscope to be distinctly prismatic.   Hence there is no doubt of the mineral being natroborocalcite.

As regards the composition of this mineral, I gave at a former page a modification of the formula originally proposed by myself, which, as at first given, was

$$NaO \, 2BO^3 + 2CaO, \, 3BO^3 + 15 \, HO.$$
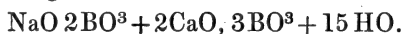
This was proved by Dr. Kraut (Chemical News, February 22, 1867) to express most correctly the results of the best analyses of the mineral by different chemists, but was objected to by Dr. Lunge (*loc. cit.*), who preferred the formula

$$2(NaO \, 2 \, BO^3) + 5(CaO, \, 2 \, BO^3) + 42 \text{ aq.}$$
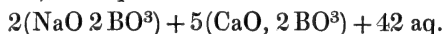
The concordance of the analytical percentages with those calculated from these two expressions is as follows :—

	Lunge.		How.	
	Calc.	Found.	Calc.	Found.
Soda . . .	5·82	5·58	7·82	7·21
Lime . . .	12·95	12·69	14·12	14·20
Magnesia		·50		
Water . . .	35·49	36·85	34·04	34·49
Boracic acid .	45·74	44·38	44·02	44·10
	100·00	100·00	100·00	100·00

In my analysis all sulphuric acid was removed by washing with cold water, a previous examination having given sulphuric acid 1·29, and magnesia 0·04 per cent.   Dr. Lunge says the mineral (he alludes probably to that from Peru) " is never found pure, but always mechanically mixed with, and often perfectly pene-

trated by, $NaCl$, $NaSO^4$, and $CaSO^4$, &c. [*sic*].   Besides, water has a decomposing action on the mineral." As regards purity, I formerly found only a trace of chlorine in addition to the MgO and SO^3 above named, and if any essential constituent had been washed out it should have been the soda; but my results certainly show no great deficiency of this. Respecting the whole constituents, on comparing the statement above given of the theoretical and actual percentages, I see no reason to abandon my formula for natroborocalcite for that newly proposed.

Probably this mineral will be found elsewhere in this district and in other parts of the province where plaster abounds; indeed, from the description of a quarryman, I have little doubt of its having been seen in another locality, unless the mineral described to me as "a stuff softer than plaster, about the size of eggs, coming clear out of the plaster and smelling like sulphur or the stones of a grist-mill," should prove to be Hayesine, a hydrated borate of lime sometimes confounded with natroborocalcite, which has not yet been found here, and which is described by Dana as having a peculiar odour: I have not perceived any odour in natroborocalcite. The other borates may of course be also expected in new localities; I have failed to find them in plaster brought to Windsor from several quarries.

Borates and other minerals, as characterizing the gypsum and anhydrite.—Of course, in addition to the interest attaching to a new member of the small class of mineral borates, and to the only known qualitative analogue of datholite, silicoborocalcite has that belonging to the first form in which combined silica has been found in the enormous deposits of sulphate of calcium here. It thus furnishes an addition to our means of learning the history of these rocks which are being shown to exhibit interesting analogies with similar formations elsewhere. I have thrown into a condensed tabular form the chief facts at present known with regard to the mineral contents of the plaster rocks in question, thus:—

Hants County, Nova Scotia, has deposits made up of

Gypsum, containing — Natroborocalcite, cryptomorphite, silicoborocalcite, glauber-salt, common salt, Arragonite, calcite, and selenite as distinct accessory minerals, and also, to be found on analysis, carbonates, partly of magnesia, and protoxide of iron, clay, and a very small quantity of silica.

and

Anhydrite, containing — Silicoborocalcite, selenite, and Arragonite, or calcite as accessory minerals, and also, to be found on analysis, carbonates, partly of magnesia, and a very little silica.

The detection of glauber-salt with the borates, and of chloride

of sodium* in gypsum of Windsor, marked a resemblance between it and similar rocks containing glauber and common salt in Spain &c., and, as regards boracic acid, with some in Germany containing boracite and Stassfurthite. Now the nodules of silicated borate in anhydrite and in gypsum of Brookville, both rocks containing a little silica, and in gypsum of Newport, bring these into the same class, so far as silica is concerned, with some gypsums (originally belonging to secondary strata) in the Hartz, which, according to Fropolli, contain nodules of silicate of magnesia, and with those of Montmartre near Paris, which hold soluble silica, or flints and chert†. Further analogy between these and other sulphate-of-calcium deposits is shown in the fact, which I have lately learned, that nearly every specimen of gypsum and anhydrite here yielding borates contains carbonates in notable but as yet unascertained amount, consisting to some extent of magnesia (of which traces appear in the borates as seen in my analyses), as well as in the detection now announced of Arragonite in cavities in gypsum, and of crusts of this mineral or calcite on the surfaces of gypsum and anhydrite, and also sometimes on the natroborocalcite and silicoborate in the former, and close to and underlying the silicoborocalcite of the latter.

These mineral contents and the numerous brine-springs of the gypsiferous districts here point to sea-water as the parent of the gypsum; but, as I observed in a former paper (1861) referred to above, ordinary sea-water would not furnish boracic acid. This acid, however, I afterwards found in a brine-spring issuing in a gypsiferous district here‡, and it has been met with in the waters of Aachen and Wiesbaden, and by Hunt in all the alkaline waters of Canada (Ontario and Quebec) examined for it, and in certain neutral waters of the same country§. These last waters arise from Lower Silurian rocks; and all those named as containing boracic acid may resemble Palæozoic sea-water rather than our own. An origin for the boracic acid in the borates has also been sought by myself ‖ in volcanic waters containing sulphuric acid, such as Dr. Dawson considers to have produced the gypsums here by action on the deposits of carbonate of lime; but when we have it combined with silica and we consider the other contents of the rocks in question, sea-water certainly seems rather to be indicated. However we may derive gypsum directly by either of these methods, or by others¶, it is said

* *Loc. cit.* 1857–61.
† Hunt, Silliman's Journal, November 1859, pp. 366, 367.
‡ Trans. Nova Scotia Institute, 1865.
§ Geology of Canada, p. 560.
‖ *Loc. cit.* 1857.
¶ See Hunt's elaborate paper " On the Formation of Gypsum, &c." Silliman's Journal, September and November 1859.

sometimes to originate indirectly from anhydrite by absorption of water. Here we must remember, as Von Cotta says, that "the supposed origin of gypsum from anhydrite leaves the greater difficulty unsolved of the original deposit of anhydrous sulphate of lime "*; and this rock we have here containing imbedded in it hydrated minerals, namely selenite and silicoborocalcite. The latter being in rounded nodules, may have been reduced to that form before being included; but the angular, lustrous, and transparent crystals of selenite cannot have been subject to action capable of so affecting a body originally angular as to render it a pebble. The nodules of hard silicoborocalcite are imbedded (so far as I observed—and I examined the accessible parts of some 300 tons of quarried rock piled in a low heap for shipment, and also saw the mineral *in situ*) exclusively in anhydrite, the soft exclusively in gypsum; there is an intermediate degree of hardness in the mineral found in a matrix composed of both these rocks. We might hence conclude that the soft results from the hard borate in consequence of physical changes accompanying the passage of anhydrite into gypsum: this is not impossible in some cases; but the gypsum holding the soft borate most abundantly is not only so much less pure a rock than the anhydrite holding the hard nodules that it could not have arisen by mere absorption of water, but there are frequently imbedded in it separate nodules of natroborocalcite, which I have never seen in anhydrite. As regards the passing of anhydrite into gypsum, what proofs are there of its ever occurring? Here we see alternations of these rocks below the surface: at Windsor, for example, large lenticular masses of anhydrite, from 2 to 10 feet thick in the centre and some 50 feet long, lie in the midst of gypsum brought to view by quarrying. In other places there are lofty cliffs composed largely of anhydrite on their surface: at Cape Canseau, for instance, I am told by Professor Lawson, the bluff, exposed to the wash of the ocean as well as the action of the atmosphere, is anhydrite, not gypsum. From a consideration of these circumstances, it appears to me that in sedimentary rocks even, where gypsum might be derived from anhydrite, but the converse is not probable, these minerals must sometimes have an independent origin. In the present case I think it must be so, because of the exclusive occurrence of the hard nodules of silico-borocalcite in anhydrite, and from the absence of natroborocalcite from this rock, while it occurs abundantly in the impure gypsum holding the soft silicoborocalcite with selenite. However these rocks and their borates may have originated, it is clear that as deposits they were contemporaneous.

* Rocks Classified, p. 292.

I am informed by Mr. Barnes that, in one locality in Cape Breton, gypsum is found containing titaniferous iron-sand; hence we may expect that, among the numerous sulphate-of-calcium deposits of the province, considerable difference will be found in the nature of their accessory minerals.

III. *Acoustic Experiments.* By A. KUNDT*.

THE great intensity with which the longitudinal tones of rods and tubes act upon our ear, and which is sometimes unbearable, though it may be partially explained by greater sensitiveness for high tones, has undoubtedly its origin in a violent agitation of the air. But as, more especially in the case of open tubes, the terminal surfaces which transmit their motion to the air are generally of small extent, the question arose as to the manner in which the transversal vibrations cooperate with the longitudinal vibrations, simultaneously with which they are formed.

Hence, at various parts of longitudinally vibrating rods and tubes, M. Kundt tried to set membranes and similar bodies in vibration by the transversal vibration of the air. The intensity in different places was also investigated by moving close over the surface of the tube one end of a caoutchouc tube, the other end of which was held in the ear; this is a method by which nodes and loops may be investigated in the case of transversely vibrating bodies.

The result was that at the sides of longitudinally vibrating bars or tubes no motion of the air could be demonstrated, and it was only perceptible at the ends, but there it had great intensity. Hence a bar clamped at the ends and set in longitudinal vibration would be incapable of communicating its motion to the air, and would therefore remain inaudible to us.

These experiments led M. Kundt to further interesting investigations.

Weber (Schweigger's *Ann.* vol. liii. p. 308) observed that a cork, which fitted one end of a glass tube several feet in length, moved from the end to the middle when the tube was held horizontally and rubbed; this was the case even when the tube became slightly narrower towards the middle, and also if, while the tube was held vertically, a column of water a few centimetres in height rested on it.

M. Kundt made the experiment with a cork ring placed on the tube, and found that the ring sometimes moved from the end

of the tube to the nearest node and sometimes in the opposite direction. If the ring, after it had moved in the direction from the end towards the node, was taken off and put on again reversed, it moved from the node towards the end. It was found that the direction in which the cork travelled depended upon its shape, so that a somewhat conical cork inside the tube always moved in the direction from the larger to the smaller basis, while a cork ring of a somewhat conical section, placed round the tube, always moved from the smaller sectional surface towards the larger one. The degree of conicity need in either case be but small. The energy of the motion is materially increased if a number of notches be made in a somewhat conical cork, so that it presents to the glass a series of conical surfaces all in the same direction. It is even sufficient to file the cork roughly, so that all the inequalities are in the same direction.

Other materials may be used instead of cork—stoppers and rings of vulcanized and of unvulcanized caoutchouc, or rolls of list; only the latter are apt to prevent the tube from sounding.

Perfectly cylindrical smooth stoppers or rings of cork or caoutchouc, on the contrary, move either not at all, or, like sand, to the nearest transverse node. This is also the case with conical and even roughly filed stoppers and rings of wood, metal, and, in general, substances of small elasticity. If any aperture (for instance a triangle) be cut with a knife in a sheet of paper, the cut surface will be nearly always conical; and when placed on a longitudinally vibrating rod, the paper moves in accordance with the law given. If the conicity is removed by smoothing the paper, it moves at most to the next transverse node.

Corresponding movements take place on longitudinally vibrating bars. Strips of plate glass 5 or 6 feet in length, were clamped and rubbed longitudinally, and the body to be investigated placed upon them. Wood, metal, and glass were observed to be passive. This was also the case with perfectly flat plane surfaces of more elastic bodies; if, however, they were roughened on the under surface, and the roughnesses were all in the same direction, they moved in the opposite direction to, or away from, the nearest longitudinal node. Most energetic was the motion of a piece of cork having a section of about a square inch, notched like a saw on the under surface, so that one surface of each tooth was normal and the other oblique to the base. The force with which this motion is effected is evident from the following experiment. Such a piece of cork as has just been described was placed upon a plate of glass, loaded with a weight of 200 grammes, and attached, by means of a string which passed over a pulley, to a scale-pan. When the strip was set in vibration, the cork moved in the direction from the vertical to the oblique section, even

when there was a weight of 200 grammes in the scale-pan. A notched cork in a tube of 6 millims. diameter could draw a weight of 70 grammes.

The author assigns as the cause of these motions the oblique propagation of the impulse of the transverse vibrations, produced by the unevennesses of the moving body, although the motion travels over the transverse nodes. As the motion ceases at the longitudinal nodes, the longitudinal vibration may exert some influence, but cannot produce the motion.

If, in order to eliminate the influence of the longitudinal vibration, a glass rod be suspended by threads in two places, and if by striking it or by drawing across it a violin-bow it be made to vibrate, a notched piece of cork moves from one end to the other in the direction indicated by the notching of the cork.

The following experiment served for the direct proof of the action of the oblique propagation of an impulse :—Through a block about a cubic inch in volume an oblique aperture was bored about 10 millims. in diameter and at an angle of about 60° to the base. The aperture was closed at the top by a metal plate in which was a small hole ; through this passed a wire fixed below to a piece of wood which accurately fitted in the aperture. Round the wire there was a spiral spring which pressed against the plate at the top and against the piece of wood in the aperture. When this apparatus was placed on a sounding rod and loaded by a weight, the spiral in the aperture was thereby compressed ; and it moved, either on a longitudinally or transversely sounding rod, always in the direction in which the spring was inclined.

That the motion oversteps the transverse nodes may be partly explained by the circumstance that the nodal lines are not fixed, but that the sand in a tube is often moved more than half an inch while it is sounding, and partly that the contact does not take place either at a mathematical point or in a mathematical line. The motion at the transversal nodes is also essentially slower than between them, and on the longitudinal nodes it entirely ceases. On transversely sounding rods the moving force of the shifting body is smaller than upon longitudinally sounding bars.

The author has made a second series of experiments, on the transference of the motion of longitudinally sounding bodies to the air, and on a method based on this principle for determining the velocity of sound in solid bodies and in gases.

If some lycopodium powder be distributed in a glass tube about 4 feet in length and $\frac{3}{4}$ of an inch wide, open at both ends, and if the tube, while held horizontally, be set in longitudinal vibration, the powder collects at the bottom in places which correspond to the spiral nodal lines. If, however, the tube be

closed by well-fitting corks, the dust, which has previously been uniformly distributed, collects no longer in those nodes of the glass, but forms a series of heaps, each of which consists of a number of fine cross lines. If the tube be again rubbed, the dust again whirls about, and, when the tone sounds, deposits again in the same manner. But if the sound be not allowed to die out slowly, but be suddenly interrupted, by rapidly rubbing the tube with a quick stroke and then suddenly clasping it with the cloth in the middle of a stroke, the same periodical accumulations of dust are observed; but the delicate ripples have disappeared, and the whole appearance of the figure is more indistinct.

These accumulations are due to permanent vibrations into which the column of air is put by the oscillations of the ends of the tubes, and which are isochronous with these oscillations. Each accumulation corresponds to half a wave-length. Sound travels in glass a little less than sixteen times as rapidly as in air. If, therefore, a tube be held in the middle while it is being rubbed, so that its length forms half a wave-length, there are sixteen accumulations of the lycopodium powder. If two corks are placed in the tube at a distance from the two ends of a quarter the length, and the tube be allowed to give the second longitudinal tone, the corks, since they are at the nodes, remain at rest, and the column of air they enclose is as little in vibration as is the air in a tube open at both ends. No dust-figures are then formed; but they immediately appear if one of the corks be again brought to the end of the tube, or placed between the two nodes. Also if there is only one cork at any vibrating part of the tube, dust-figures are obtained; yet the motion of the air is most energetic if both ends are closed. To produce dust-figures, it is unnecessary that the column of air be a whole multiple of half a wave-length; yet the ease with which the figures are produced, as well as their form and regularity, appears to depend on the ratio of the length of the sound-wave to that of the column of air.

The following is adduced as a characteristic property of the figures of frequent occurrence. Let a tube in which lycopodium powder is as uniformly distributed as possible, be rubbed with a stroke which is not too powerful. Accumulations of dust are then met with, very beautifully formed of ripples; between every two of these accumulations there is a circular or elliptical space which is tolerably free from dust, and is surrounded by a delicate ring of dust. These rings or holes are largest at the nodes of the longitudinal motion of the tube, and diminish in size towards the middle between two nodal points.

Sand or other heavy bodies are not moved by the waves of air in the sounding tubes.

These dust-figures furnish a convenient means for determining the velocity of sound in solids and in gases.

Since the velocity of sound in air is known for a given temperature, from the distance of corresponding places of two successive heaps of dust, which is equal to half the length of the sound-wave, we get the number of vibrations of the tone of the column of air, and, as this tone is the same as that of the tube, the number of vibrations of the material of the tube. Conversely, from the known velocity of sound in the material of the tube, the velocity of sound in an enclosed gas may be calculated from the observed length of the enclosed gas. In tubes in which the velocity of sound is equal, and which are filled with different gases and held in the middle while being rubbed, the velocities of sound in the gases are inversely as the numbers of heaps of dust. This mode of determination is sufficiently accurate. But the desire to get still more accurate results, and to be able to determine the velocity of sound in solids, led M. Kundt to produce the dust-figures, not in the sounding tube, but in an adjacent column of air. Over the closed end of a glass tube a few feet in length, a somewhat wider glass tube was pushed to a distance of a quarter the length of this closed tube, and was here firmly fixed by a cork. At the other end of the outside tube was a cork, which by means of a rod could be moved backwards and forwards. If now the first tube, by which the apparatus is held in the hand, be rubbed in the middle so that two nodes are formed, the vibrations of the closed end set in motion the air of the tube surrounding it, and produce a series of dust-figures the lengths of which are to the length of the rubbed tube as the velocity of sound in the gas is to that of the material of the tube. If instead of the first tube any rod be taken which can excite sound, the quotients of the lengths of the sounding body by the distances of corresponding points of successive divisions of the dust-figures are as the velocity of sound in the sounding body. The figures thus obtained are far sharper than those in the sounding tubes, and therefore permit a more accurate measurement. According to the ratio of the length of the sounding column of air to the semiwave-length, the dust-figures may materially differ in form. If, while the inner tube is sounding, the cork at the end of the outer be moved backwards or forwards, a place is soon found at which the whole of the lycopodium in the tube collects in small heaps at equal distances from each other, the extreme heap just touching the moveable cork. Each of the heaps is at an air-node, and the space from the moveable cork to the end of the sounding tube is divided by them (when they are formed) into a number of exactly equal parts, so that the length of the column of air is the exact multiple of half a wave-length. If

there is not too much lycopodium in the tube, the heaps are very sharp and well defined, so that their distances can be measured with great accuracy. If by pushing the cork the length of the column of air be altered by half a wave-length, a totally different dust-figure is obtained—that is, the dust-heaps which form in sounding tubes at the nodes each being separated from the next by an empty space surrounded by a ring. One of the nodes is always at the moveable cork.

The shape of the dust-figures seems always to depend on the intensity of the vibrations of air; for when the external tube is considerably wider than the sounding one, and thus the end which produces the motion small as compared with the section of the column of air, the heaps of dust are not formed, but the figure with the holes. When the tone is feeble, the figure with the holes appears first, and it is only gradually on continued sounding that the dust accumulates in heaps. It would seem to follow from this that the intensity of the motion of the air is considerably greater if the column of air is an entire multiple of half a wave of air than if this is not the case. And in fact the oscillation in the loops must be greater the nearer the tone-exciting terminal surface, with its given amplitude of oscillation, is to a node. In agreement with this, sand or another heavy powder would not move at all in the tube if the dust-figure with the holes is formed. But if the apparatus is so arranged that the dust collects in heaps at the nodes, if pure quartz sand be also present, this is violently moved and forms accumulations between the heaps consisting of extremely regular ripples of sand, while it rests at the nodes or sometimes forms holes similarly to the lycopodium. It would thus appear that the intensity of the motion of the air which is sufficient to collect the lycopodium dust in heaps, can only arrange sand in such a form as lycopodium assumes when the motion of the air is less intense. In all modifications and transitions of the dust-figures, the distance of two successive similar points is equal to half a wavelength.

M. Kundt has executed a series of measurements for determining the velocity of sound in various bodies. In the case of solid bodies, the results show that the method is capable of great accuracy.

The bar in which the velocity of sound was to be determined was mostly fastened at two nodes; and over one of its free ends the glass tube for the dust-figures was pushed. The ratio of the length of one dust-heap to half the length of the bar was then the ratio of the velocity of sound in the air to that in the bar. The length of the bar could be measured with great accuracy. The lengths of a great number of beautifully formed dust-waves

were measured with a pair of compasses, and the mean taken of 5–10 measurements.

I. *Steel.*—Three steel bars, of the same kind of steel as far as could be ascertained, were used: one was 1002·7 millims. in length and 10 millims. in thickness ; the two others were 5 millims. thick and 1001·7 millims. and 501 millims. long respectively. Taking the the velocity of sound in air as unity, they gave the velocities respectively

<p style="text-align:center">15·325, 15·334, 15·343.</p>

II. *Brass.*—A brass rod, about a metre long and 5 millims. thick, gave, in three successive experiments,

<p style="text-align:center">10·88, 10·87, 10·86.</p>

A second, similar one gave

<p style="text-align:center">10·94,</p>

and, with a dust-tube not closed at the end,

<p style="text-align:center">10·90.</p>

III. *Glass.*—A thin glass rod gave, in three successive experiments,

<p style="text-align:center">15·24, 15·25, 15·24.</p>

IV. *Copper.*—For a copper wire above a foot in length there was obtained

<p style="text-align:center">11·966</p>

Wertheim found for cast steel 14·961, for steel wire 15·108, for copper 11·167, numbers which agree with the above as accurately as can be expected from the difference of the materials.

In the case of gases the author did not use the external tube, but filled different tubes with different gases and counted the dust-figures produced. There is thus obtained an easily reproduced image of the various velocities of sound, whose ratio can only be obtained approximately by counting, yet with sufficient accuracy.

On an entire glass wave the number of half waves of the gas was—

<div style="text-align:center">

Carbonic acid . . . 40
Air 32
Coal-gas 20
Hydrogen . . . 9

</div>

Taking the velocity of sound in air as unity, we get the following velocities for different gases :—

<div style="text-align:center">

Carbonic acid . . . 0·8
Coal-gas . . . . 1·6
Hydrogen . . . . 3·6

</div>

Wertheim finds 0·79 for carbonic acid and 3·81 for hydrogen.

A tube filled with air through which ether had passed gave 35 waves instead of 32 ; that is, 0·91 for the velocity of sound in air saturated with ether.

The following experiment was made on the influence of temperature on the velocity of sound. The apparatus with two glass tubes gave as the mean of several measurements 35·743 millims. for the length of half an air-wave at 14° C. When the outside tube was heated to about 26° C., 36·576 millims. was found to be the length. A new determination at 14° gave again 35·797 millims., while at 30° 37·357 millims. were found.

Warming the sounding glass tube had thus scarcely any influence on the length of the air-wave, and thus left almost unaltered the velocity of sound in glass.

IV. *On certain Lecture-experiments, and on a New Form of Eudiometer.* By JOSIAH P. COOKE, Jun., *of Harvard College**.

THE laws of combination by volume fill such an important place in our modern chemical philosophy, that simple methods of illustrating these fundamental principles in the lecture-room are eagerly sought by every teacher of the science. The many new and interesting experiments devised for this purpose by Professor Hofmann, first described in the Journal of the Chemical Society of London (Ser 2. vol. iii. p. 156), and subsequently made still more widely known through his admirable 'Introduction to Modern Chemistry,' leave little to be desired so far as regards accuracy of results or elegance of illustration. But these experiments require for the most part a delicacy of manipulation which is incompatible with the hurry of the lecture-room, and a skill in glass-blowing which can rarely be attained. Hence, while seeking the same end as Professor Hofmann, but with less ample appliances, the author has devised for his own lecture-room methods of illustrating the same principles, which require less delicate apparatus and less careful attention, although as analytical methods they may not always be as accurate as those of that eminent chemist.

Many of the methods described in this paper are alone rendered possible by the application of vulcanized rubber stoppers in the construction of the required apparatus. Hitherto these have not been made of good quality in this country ; and those imported from Europe were very costly, and could only be ob-

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* From a separate reprint from Silliman's *American Journal*, communicated by the Author, to whose kindness we are also indebted for the woodcuts.

tained of a few invariable sizes. At the suggestion of the author, the "Boston Belting Company" now manufacture an excellent article, which they call "stopper-cord," consisting of conical rolls of very elastic rubber about 4 feet in length and varying in diameter from $\frac{1}{2}$ an inch at one end to $1\frac{1}{2}$ inch at the other *. From these rolls stoppers of any required size between the limits named may be cut with an ordinary knife and bored with a common brass cork-borer. It is only necessary to moisten the tools with water in order to prevent the adhesion of the rubber. Stoppers of this material are absolutely air-tight even against a full atmospheric pressure, provided that the surface of adhesion to the glass neck is at least half an inch in length.

Another material of prime importance in these experiments is sodium-amalgam, which is most conveniently used when containing so large an amount of sodium as to form a hard solid. It is best prepared by gently heating a few ounces of metallic mercury in a shallow iron dish and then cautiously adding one-twentieth of its weight of sodium. The first half of the sodium should be added in very small portions at a time, as the action at the beginning is exceedingly violent, but soon moderates; and at last the melted amalgam must be stirred with an iron spatula in order to incorporate thoroughly the materials. As soon as cold, the solid amalgam readily separates from the dish, and should then at once be broken up into small fragments and preserved in a well-stoppered bottle.

The four great typical compounds of modern chemistry are HCl, $H^2 O$, $H^3 N$, and $H^4 C$. Excepting the last, for which we have no new methods, we will now describe our methods of illustrating the composition of each of these in turn.

Hydrochloric acid.—The points to be illustrated in the case of this gas are all indicated by the equation

$$\boxed{H} + \boxed{Cl} = \boxed{H\,Cl}$$
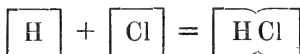
or by the molecular expression

$$\boxed{H\;H} + \boxed{Cl\,Cl} = \boxed{H\,Cl \mid H\,Cl}$$
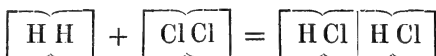
* After a good deal of experience, rolls of the sizes named above have been found to be the most universally applicable; but they can be made to order of any desired dimension and at a cost not exceeding one dollar a pound. See fig. 5, where one of these rolls is shown in the foreground of the woodcut.

The first fact, that HCl consists of hydrogen and chlorine gases, we prove by the electrolysis of strong liquid hydrochloric acid, having previously shown in the course of the lecture how HCl is obtained from common salt, and that the liquid acid is merely a solution of the gas in water. The decomposing cell which we use in this experiment is represented in outline by fig. 1, which is drawn to a scale of one-fifth, so that both its construction and dimensions require no detailed description. The two small open glass cylinders are fitted by grinding with emery to the two tubulatures of the cell, and when the instrument is not in use are closed above with ground glass stoppers. When mounted for use, the cell is filled with strong hydrochloric acid to within an inch of the upper
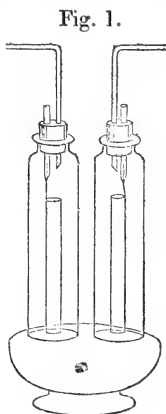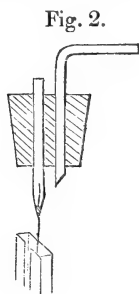
Fig. 1.   Fig. 2.

mouths of the cylinders, and the glass stoppers are replaced by rubber stoppers through which pass the gas-delivery-tubes and the conducting-wires connecting with the electrodes, which are two strips of platinum-foil 4 inches long by 1 inch wide. The platinum conducting-wires are welded* to the strips of foil and secured in the rubber stoppers as represented in detail by fig. 2. Into the lower end of a short piece of glass tube, which passes tightly through the rubber, the platinum wire connecting with the foil is secured by melting the glass around it, while the upper end is left open to receive the copper conducting-wires from the battery, and the connexion is made perfect by placing a few drops of mercury in the tube. This simple form of connecting-cup is easily made and very convenient.

As the conducting-power of hydrochloric acid is very good, three Bunsen's cells of the ordinary size have ample intensity and give a rapid evolution of gas. The hydrogen gas is conducted into a tall but narrow glass jar mounted in the usual way over a small pneumatic trough, while the chlorine is col-

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* The platinum wire is very easily welded to the foil on a smoothed surface of a lump of quicklime which serves as an anvil. The two, having been placed together in the required position on this support, are first intensely heated at the points to be united, with a blowpipe-flame, and then a quick blow with a small hammer completes the work.

lected by displacement in a precisely similar jar mounted as represented in fig. 3. The mouth of this jar is closed by a ground glass plate which is tubulated, as is shown in detail by fig. 4. This tubulature, again, is closed by a rubber stopper through which pass, first the delivery-tube, which reaches the bottom of the jar, and secondly an overflow tube, which merely passes through the stopper, and which in the experiment should be connected by a flexible hose with a ventilator. When a larger amount of chlorine is desired, the first jar may be connected

Fig. 3.   Fig. 4.

with a second, and that with a third, &c., all mounted in the same way, and the exit-tube from the last jar leading to a ventilator as before. When the jars are full, the tubulated stoppers with their connexions are removed and a plain glass cover substituted. This simple form of apparatus will be found very useful in all experiments on gases heavier than the air.

During the process of electrolysis the class will see that the two gases are evolved in nearly the same proportions, the coloured gas rising in one jar as rapidly as the water falls in the other. The narrowness of the jar prevents to a great degree the diffusion of the chlorine; and a piece of white paper placed behind the jar will make the line between the coloured gas and the air visible to a considerable distance. When the jars are full, the qualities of the two gases may be made evident by appropriate experiments. As is well known, the gases will not be delivered in atomic proportions until the liquid acid is saturated with chlorine. It is best, therefore, not to empty the cell after the experiments, but, having removed the rubber stoppers with their attachments, to close the mouth with the ground glass stoppers, and the apparatus will then be ready for the next occasion. It is also best to interpose a small wash-bottle containing sulphuric acid between the cell and the chlorine-jar; for this will not only dry the gas, but also equalize the hydrostatic pressure on the two delivery-tubes. Decomposing-cells like that represented in fig. 1, and all other forms of glassware described in this paper, are made by the New England Glass-Company of East Cambridge, and can be ordered through any of the
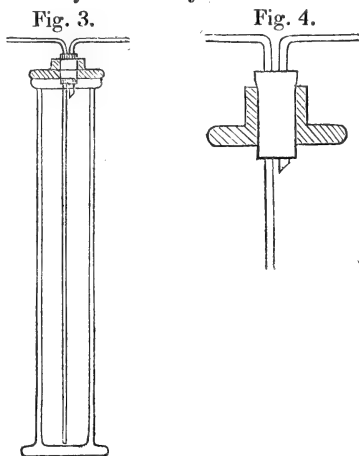
dealers in philosophical apparatus in Boston.   A much simpler
decomposing-cell, although not quite so efficient an apparatus,
can be made with a common U-tube supported on a wooden
stand and mounted with rubber stoppers, delivery-tubes, and
platinum electrodes in every respect like the other.

The second point to be illustrated in regard to hydrochloric
acid is, that it consists of equal volumes of its constituent gases;
and although by our first experiment, if made in the way we
have described, it is shown that the gases are evolved in nearly
equal proportions, yet a second experiment is required to esta-
blish the absolute truth* of this important fact.   The apparatus
we use for this purpose is represented in fig. 5, and the details

Fig. 5.   Fig. 6.
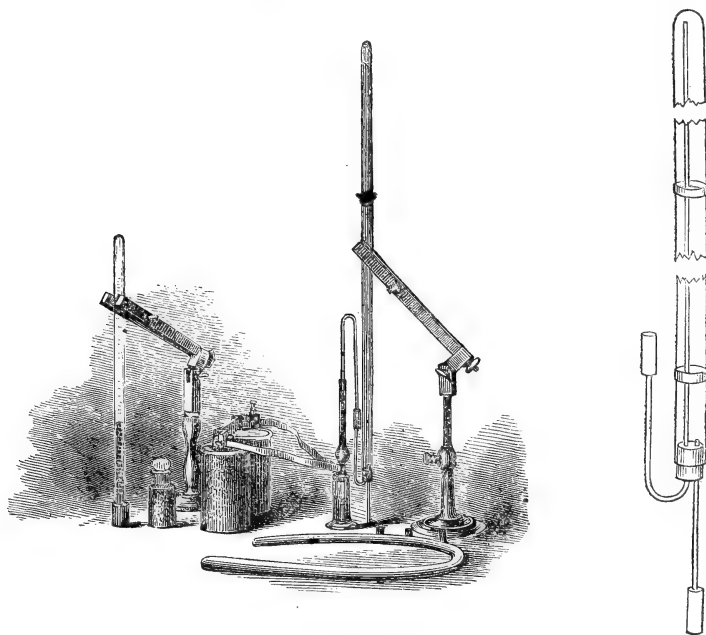
of the several parts are shown in fig. 6.   The two gases are

* We here of course leave out of view the small difference which arises
from the fact that the gases do not absolutely obey Mariotte's law, and are
therefore unequally condensed even by the atmospheric pressure.   The
volumes of the two gases would undoubtedly be exactly equal under greatly
diminished pressure; but under the pressure of the air the volume of the
molecular weight of chlorine is about $\frac{1}{100}$ less than the corresponding volume
of the molecular weight of hydrogen, a difference by no means inappreciable
in accurate experiments.

evolved together from a simple decomposing-cell, shown more
in detail in fig. 9, but in connexion with another apparatus; and
the connexion of the battery with the two electrodes is here
made as before shown in fig. 2.   The mixed gases pass through
a small drying-tube filled with pumice moistened with oil of
vitriol into an absorption-tube whose construction is shown in
detail by fig. 6.   As the gaseous mixture is decidedly lighter
than air, it is conducted to the top of the absorption-tube through
the small quill-tube, and overflows through the short tube
below.   Both of these should pass air-tight through the rubber
stopper which closes the mouth of the large absorption-tube, and
which should therefore have a bearing on the glass of at least
half an inch.   It will be noticed that, while the overflow-tube
is straight, the delivery-tube is bent so that its open end is four
or five inches above the mouth of the absorption-tube.   Rubber
stoppers, or rather caps, must also be provided, by which the
open ends both of the delivery- and the overflow-tubes may be
closed at the right time.   These are made by boring with a cork-
borer *nearly* through an ordinary stopper, and then pulling out
the rubber core with a pair of pincers.   The absorption-tube
should now be divided into two parts of equal capacity by means
of rubber rings, having, however, a length of three or four inches
at the lower end for the absorbent liquid.

The absorption-tube having been prepared as described and
filled with the mixed gases, the experiment is made in the fol-
lowing way :—The apparatus is first rapidly depressed in a solu-
tion of caustic soda (of the ordinary strength used in the labo-
ratory) until the liquid rises in the tube to the level of the first
ring.   The open end of the delivery-tube is now quickly closed
with the rubber cap, and then the end of the overflow-tube is
closed in the same way, the second rubber cap having been pre-
viously dropped upon the bottom of the glass vessel containing
the soda solution so as to be ready for the purpose.   The tube,
now perfectly air-tight, is removed from the liquid, and the solu-
tion of soda turned backward and forward through its entire
length until the chlorine is wholly absorbed.   The end of the
overflow-tube is now opened under water coloured blue with
litmus, which, as it rushes in, will be instantaneously bleached,
indicating the presence of chlorine.   The tube must now be
immersed in the water until the level of the liquid is the same
within and without, when it will be found that just one-half of
the gas has been absorbed.   We have now proved that one-half
of the volume of gas evolved during the electrolysis of hydro-
chloric acid consists of chlorine, and it only remains to show
that the remaining half still left in the tube is hydrogen.   For
this purpose the delivery-tube may be connected with a water-

faucet and the gas burnt as it is forced out through the over-flow-tube.

We have now proved, first, that hydrochloric acid is composed of hydrogen and chlorine, secondly, that these gases are present in equal proportions by volume; and in order to complete our demonstration of the constitution of this typical compound, we have only to prove that when these equal volumes unite to form HCl there is no condensation. This we may do either synthetically or analytically.

The synthetical experiment is made by filling the absorption-tube as before with the mixed gases obtained by the electrolysis of hydrochloric acid, taking great care, as also in the previous experiment, that the tube shall be perfectly dry. It will of course be necessary to have two of these tubes if both experiments are to be made in the same lecture. The tube thus filled is to be exposed for some time to bright diffused sunlight, and afterwards directly to the sunbeam until perfect combination results. If the glass is quite thick and the rubber stopper is forced in very tight, the gases may even be exploded in the tube without danger, although this form of the experiment is always attended with some risk. When the gases are in either way thoroughly combined, the end of the exit-tube is first opened under mercury, in order to prove that no condensation has taken place, and afterwards under water coloured blue by litmus, when a very rapid absorption takes place, and the red-dening of the water will indicate that HCl has in fact been formed.

The analytical experiment is made by decomposing HCl gas by means of sodium-amalgam. For this purpose the carefully dried gas is first collected over mercury in a perfectly dry tube. This tube we assume is graduated, or at least divided into two parts of equal capacity. The tube full of gas is now slipped over the mouth of a rubber cap, which has been previously filled with the amalgam (see fig. 5, left side of the woodcut), and sunk in the mercury-trough until the liquid is just level with the brim. This cap, which is easily made from the " stopper-cord," should be capable of holding 10 or 20 cubic centims. of the amalgam, and should tightly clasp the tube. Moreover, for this purpose, the solid amalgam above described should be reduced with mercury to the consistency of a thin paste. The amalgam is now to be shaken up in the tube for several minutes until the decomposition is complete, and then the mouth of the tube may be opened under mercury. The liquid will rise to supply the place of the chlorine which has been absorbed; and on sinking the tube in the mercury-trough until the level is the same within as without, it will appear that exactly one-half of

the volume has disappeared.   As this, however, would require a deep cistern of mercury, and as the interior surface of the tube is left in such a very dirty condition as to obscure the result, we prefer to transfer the tube to a jar of water, which, when the cap is removed, at once displaces the mercury and washes out the interior without sensibly impairing the accuracy of the experiment.

Water.—The points to be illustrated in the case of water, or rather of free steam, are all indicated by the equation

$$\boxed{\text{H H}} + \boxed{\text{O}} = \boxed{\text{H}^2\text{O}}$$
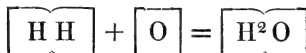
There is no more striking experiment in this connexion than the decomposition of water by sodium, but as made in the usual way the experiment is attended with no little danger.   Sodium in certain states explodes violently when brought into contact with water; and after several accidents of this sort we have substituted the solid sodium-amalgam above described with the best results. We place an ounce or more of this amalgam in a common gas-flask and pour upon it water.   The action is very moderate and must be assisted by a gentle heat; but on heating the flask with a gas-lamp the gas is evolved rapidly and with great regularity. We collect it over the pneumatic trough, and illustrate its properties in the usual way.

We illustrate the fact that water is composed of two volumes of hydrogen to every one of oxygen by the electrolysis of dilute sulphuric acid, using for the purpose the decomposing-cell (fig. 1) already described. We collect the gases in two tall bell-glasses standing side by side on the shelf of the same pneumatic trough.   These bells are of course calibrated, and the equal divisions marked by rubber rings.   Six cells of Bunsen's battery, medium size, give a rapid evolution of gas.

Lastly, we illustrate the fact that, when the elementary gases unite to form aqueous vapour, three volumes are condensed to two, by means of the eudiometer represented in fig. 7.   This apparatus is easily made with a common iron casting, well known to steam-fitters as a "return bend."   Any machinist will easily adapt this casting to the required use by attaching to it, as shown in the figure, a circular iron plate to serve as a stand, by

Fig. 7.
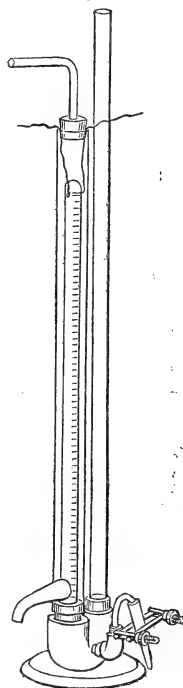
also screwing on to one side an ordinary "elbow-joint," and at the same time by carefully rimming out the three apertures so as to present smooth surfaces for the adhesion of the rubber stoppers.   Into one of the openings of the "return bend" we fasten with a perforated rubber stopper a common straight *eudi-ometer-tube* (such, for example, as is ordinarily used in Bunsen's method of gas-analysis), while into the second opening we fasten in a similar way an *open* glass tube.   In the opening of the elbow-joint we secure with a perforated rubber stopper as before, that convenient substitute for a stopcock so well known to che-mists as a nipper-tap.   Last of all we obtain from the glass-house a tubulated tube, like that shown in fig. 8, of such size that it will cover the eudiometer-tube and fit the

Fig. 8.

upper end of the same rubber stopper by which the last is secured in its place.   The upper end of this *outer tube* is also closed with a perforated stopper, as shown in the figure; and fine platinum wires connecting with the wires of the eudiometer pass between the stopper and the glass.   The lower end of the outer tube should not fit too tightly around the rubber stopper, so that it can easily be removed when not wanted; moreover all the stoppers should be made of such length that, while perfectly tight, they can easily be re-moved for cleaning the tubes*.   These rubber joints, if well made, give great flexibility to the ap-paratus, and enable it to withstand quite rough usage.

The eudiometer being thus mounted, mercury is first poured into the open limb, which is then closed with a rubber stopper and the mercury transferred by inclining the apparatus to the closed limb, this process being repeated until the eudiometer-tube is full.   The excess of mercury is now drawn out of the open tube by the tap, and, this tube having been re-moved, the instrument is left as represented in fig. 9.   The eudi-ometer is now ready for receiving the mixed gases, which are passed up into it from a simple decomposing-cell, as shown in the figure, the excess of mercury overflowing into any conve-nient vessel.   The *open tube* is now replaced, and the outer tube

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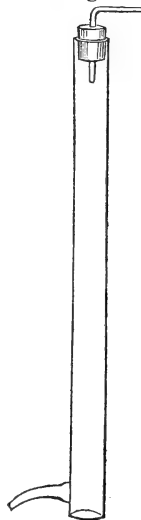
* It is also best to place around the upper end of the eudiometer-tube a rubber ring, quite narrow, but sufficiently thick to fill the annular space when the outer tube is in its place, and also perforated with a number of small holes, so that the steam or vapour employed in the experiments may pass freely.   This ring confines the eudiometer-tube and gives greater so-lidity to the apparatus.

secured in position. It is next necessary to raise the temperature of the eudiometer-tube to a point considerably above the boiling-point of water, and maintain it at this temperature during the rest of the experiment. This is most conveniently done by passing through the *outer tube* the vapour of amylic alcohol (fousel oil), which may be generated in a flask placed at one side and connected by a glass tube with the upper end of the apparatus. The tubulature at the lower end of the tube should at the same time be dipped into the mouth of a glass bottle into which the alcohol may flow as fast as the vapour is condensed; and since the latent heat of this vapour is very small, this simple method of condensation will be found amply sufficient.

Fig. 9.

As soon as the temperature of the eudiometer-tube is constant, which can easily be told, because the mercury-column will then remain at a constant height, mercury must be poured into the open tube or withdrawn from it by the nipper-tap until the level is the same in both limbs of the apparatus. It remains now only to note the volume of the confined gas, and to explode it by passing an electric spark through the platinum wire already noticed—first, however, tightly closing the end of the open tube with its rubber stopper. When the stopper is removed and the mercury-columns again brought to the same level, it will be found that the volume of the confined gas has been reduced one-third. The result, however, is always a little too small, because aqueous vapour, even at the boiling-point of amylic alcohol (132° C.), does not exactly obey Mariotte's law, and is somewhat more condensed than the mixed gases by the atmospheric pressure. It would be better to employ the vapour of a liquid having a still higher boiling-point; but the results with amylic alcohol are sufficiently accurate for a lecture-experiment*.
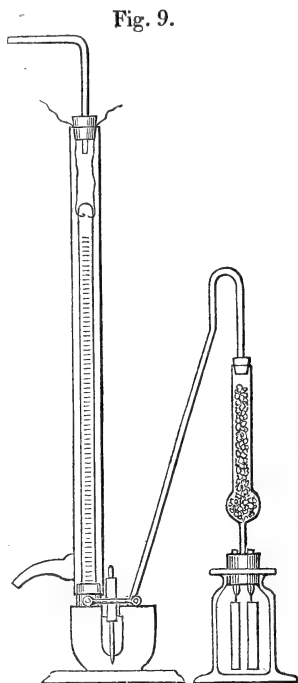
* Indeed we can obtain with free steam a result which is sufficiently near the theory for all purposes of illustration; only it is then important that both the mixed gases and the resulting vapour should be measured under

Ammonia.—The points to be illustrated in the case of ammonia are indicated by the equation

$$\boxed{\text{H H H}} + \boxed{\text{N}} = \boxed{\text{H}^3\text{N}}$$
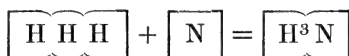
We demonstrate the composition of ammonia by the old methods, which are familiar to every teacher, synthetically by passing a mixture of nitric oxide and hydrogen over heated platinum-sponge as in the beautiful experiment of the late Dr. Hare, and analytically by decomposing aqua ammoniæ either by electrolysis or by means of chlorine. For the electrolysis of ammonia the decomposing-cell (fig. 1) may be used, filling it with the strongest aqua ammoniæ and adding a not too small amount of sulphate of ammonia in order to increase the conducting-power of the liquid. The reaction is less simple than in the electrolysis either of water or of hydrochloric acid; but as the final result the gases are evolved, very nearly at least, in atomic proportions, three volumes of hydrogen to one of nitrogen. They can be collected separately in graduated bells as in the electrolysis of water. In decomposing ammonia by chlorine, we use with very satisfactory results the apparatus shown in fig. 6, and already described. For this use, however, a tube should be selected so thin that water may be boiled in it without risk of breaking the glass. The tube having been filled by displacement with pure and dry chlorine gas, we press down the lower end into very weak aqua ammoniæ (eight measures of water to one of the concentrated solution) until the liquid, flowing in through the overflow-tube, rises to the height of the first rubber ring. We now quickly close the delivery-tube with its rubber cap and allow the absorption to continue until the tube is about half full of the ammonia-water, when we also close the overflow-tube and shake up the liquid in the large tube until all cloudiness has disappeared from the interior. The decomposition is now complete; but a considerable amount of the liberated nitrogen still remains dissolved in the liquid. To expel this we heat the tube carefully over a gas-lamp until the liquid within begins to boil. On now transferring the apparatus to the pneumatic trough and opening the overflow-tube under water, it will be found, when the tube cools, that just one-third of the original volume is left, and it can easily be shown that the residual gas

a pressure considerably less than that of the atmosphere. For this purpose a long eudiometer-tube should be used, and before each measurement the level of the mercury should be adjusted so that it shall stand in the open tube from 10 to 15 inches lower than in the eudiometer. Of course the difference of level must be the same at both measurements.

is nitrogen.   Hence it follows, since chlorine always combines with its own volume of hydrogen, that ammonia contains only one volume of nitrogen to every three volumes of hydrogen, the point to be proved.   To complete this series of illustrations, it only remains to show that in ammonia-gas the four volumes are condensed to two.   For this pupose some dry ammonia-gas is passed up into the eudiometer-tube as in fig. 9.   The side tube is then replaced as in fig. 7, the mercury-level adjusted, and the position marked with a rubber ring.   A stream of electric sparks from a Ruhmkorff coil is now passed through the gas, so, arranging the connexions that the sparks may traverse the whole length of the gas-column ; and the amount of gas should be small enough to render this possible.   The decomposition proceeds somewhat slowly ; but, after sufficient time, on readjusting the level it will be found that the volume of the gas has doubled.   Besides the experiments described above, there are many others to which these same forms of apparatus are applicable ; but these will suggest themselves to every teacher, and therefore it is not necessary to enter into further details.

Eudiometer.—The eudiometer described above, although originally contrived for the lecture-table, has proved to be of still greater value in the laboratory in all processes of gas-analysis for which such an instrument is required.   It is not only very cheap, simple, and easily repaired, but also equally as accurate as the most complicated apparatus.   It can be used in a room of the most variable temperature; for, by passing a current of water or of steam, as the case may require, through the outer tube, the temperature of the eudiometer-tube may be easily maintained absolutely constant.   The various gases are passed in as shown in fig. 9, and through the same opening the reagents used in the processes of analysis are readily introduced.   By replacing the open tube, as in fig. 7, and bringing the two mercury columns to the same level, the residual volumes may always be read off under the atmospheric pressure and at a constant temperature, indicated by a thermometer placed in the annular space between the tubes.   Or, on the other hand, by varying the height of the mercury-column in the outer tube, we may reduce the gas to the same volume and measure the difference of tension according to the method of Regnault.   This form of eudiometer is especially adapted for the admirable methods of gas-analysis devised by Bunsen.   The absorbent balls used by him are most readily introduced when the apparatus is arranged as shown in fig. 9 ; and the volume of aqueous vapour formed after combustion may easily be measured by replacing the current of cold water through the *outer tube* by a current of free steam.   In this case it will be best to measure the gas under as great a dif-

ference of pressure as possible, in order to ensure that all the water is vaporized, and also in order to avoid the somewhat uncertain correction arising from the difference of temperature of the two limbs of the apparatus. This correction, which in most cases is insignificant, becomes important when steam is used; and it is then best to measure directly the difference of level between the mercury in the open mouth of the iron cistern (fig. 9) and that in the tube. This we do by the millimetre divisions on the eudiometer-tube with the aid of a very simple contrivance. A split ring of blackened sheet brass carrying a bent steel wire is slipped down over the outer tube until the end of the wire just touches the surface of the mercury. The vertical height of this simple measure being known, we have only to add to it the height of the mercury-column above the upper edge of the ring in order to know the exact difference of level. Of course care must be taken when the measurement is made that the mercury-column is vertical; but it is unnecessary to dwell on such obvious precautions, which are essentially the same with this apparatus as those so fully detailed by Bunsen in his work on ‘ Gasometry.’ It is obvious, moreover, that the number of these corrections is considerably diminished in using this apparatus as compared with the ordinary mercury pneumatic trough; and besides the convenience and comfort of working in a warm room, it has the additional recommendation that it requires a very small amount of mercury.

The above apparatus, as represented in fig. 9, may also be used with great advantage in Gay-Lussac’s process of determining the density of vapours. The method of using it is obvious to any one who is familiar with the process. After a weighed amount of the liquid under examination, enclosed in a thin glass bulb, has been passed up into the eudiometer-tube, it is readily converted into vapour by passing steam, or the vapour of some liquid of a still higher boiling-point*, through the outer tube. All the measurements required in the determination are now easily made. The temperature is measured by a thermometer placed in the annular space between the two tubes; and the difference of level of the mercury in the two limbs of the instrument may be most accurately determined by means of a cathetometer, aided by the simple contrivance just described.

* Hydrocarbons of high but still constant boiling-points, obtained by the methods of Mr. C. M. Warren, might be used with proper precautions in such determinations.

V. *On a remarkable Phenomenon observed at Rangoon.* *By* Dr. C. Collingwood, *F.L.S.**

I ACCIDENTALLY heard mention by an eye-witness (a lady residing at Hong Kong) of a circumstance which struck me as so remarkable and interesting that I collected the particulars with care, allowing the narrator to tell her own story, and filling up important particulars by putting questions as little as possible calculated either to lead or mislead.

It was in the year 1846 that she was on board her husband's ship the 'Manook,' in the Rangoon River, and was walking up and down the poop in company with the chief mate and a child four years old, the poop awning being at the time spread overhead. It was about half-past 7 in the evening, and then quite dark, when suddenly, without any warning, a tremendous sheet of light appeared to rush across the bows of the vessel in a horizontal direction. The light was not like lightning, but appeared to pass swiftly along, and had the aspect of a red thick flame, occupying the whole space left visible between the awning and the ship. The suddenness and terrific nature of the glare was such that she fell down upon the deck, believing, as she expresses it, that the world had come to an end, while the child screamed aloud with terror.

As this frightful luminous appearance rushed by the ship a considerable accession of heat was felt by both the adult persons, and a strong sulphurous smell also accompanied it, though how long this feature lasted cannot now be stated with any certainty. But the phenomenon was unaccompanied by any sound, and sped noiselessly on ; nor could they see where it went, or what finally became of it. The whole affair lasted but some seconds, the light having dashed past them with a speed only inferior to lightning.

The captain of the ship, and Captain Brown, postmaster and only European resident at the time, were in the house of the latter, situated but a short distance from the shore and from the ship. They both averred that they felt a sudden and remarkable heat, although they saw no light ; and when told of the circumstance afterwards, on comparing notes as to the time, they immediately exclaimed words to this effect, " Then that explains the sudden and unaccountable warmth we felt at that time."

It is worthy of remark that my informant spontaneously stated that, as well as she could recollect from collateral circumstances this must have occurred some time during the month of November.

* Communicated by the Author.

The two gentlemen on shore are both dead; but the mate is believed to be still living. It was often a matter of wonder to them that an occurrence which to them appeared so extraordinary was never publicly noticed; but it seems that they were the only Europeans who observed it, as I learn that, besides the natives of the place, the only other residents at that time were Armenians.

The whole account which I have been able to gather of this phenomenon so closely agrees with the description given of that class of meteors known as silent fireballs, or bolides, that I feel convinced that my informant must have witnessed one of these bodies in terrific proximity; and as I am not aware that any one has ever recorded such an experience, I have thought it worth while to draw up this *procès verbal,* to which my informant has attached her sanction.

When at Dundee I was much struck by Mr. A. Herschel's concluding experiment, which represented a silent bolide, and considerably startled the audience by its noiseless flash across the back of the hall. The gliding light and the accompanying heat forcibly recalled to my recollection the particulars I had gleaned of the Rangoon phenomenon.
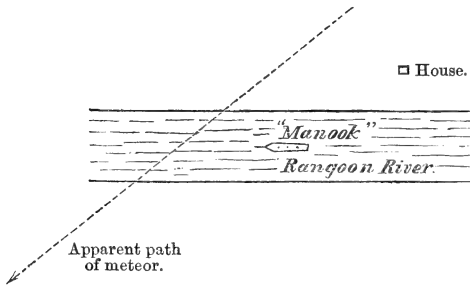
The above plan will assist in giving an idea of the relative position of the ship, house, and meteor.

VI. *On a Uniform-Electric-Current Accumulator.*
By Sir William Thomson, *LL.D., F.R.S.*[*]

CONCEIVE a closed circuit, C T A B C, according to the following description:—One portion of it, T A, tangential to a circular disk of conducting material and somewhat

longer than the radius; the continu-
ation, A B, at right angles to this in
the plane of the wheel, of a length
equal to the radius; and the completion
of the circuit by a fork, B C, extend-
ing to an axle bearing the wheel. If
all of the wheel were cut away except
a portion, C T, from the axle to the
point of contact at the circumference,
the circuit would form a simple rect-
angle, C T A B, except the bifurcation of the side B C. Let a fixed
magnet be placed so as to give lines of force perpendicular to the
wheel, in the parts of it between C the centre and T the point
of the circumference touched by the fixed conductor; and let
power be applied to cause the wheel to rotate in the direction
towards A. According to Faraday's well-known discovery, a
current is induced in the circuit in such a direction that the
mutual electromagnetic action between it and the fixed magnet
resists the motion of the wheel. Now the mutual electromag-
netic force between the portions A B and C T of the circuit is
repulsive, according to the well-known elementary law of Am-
père, and therefore resists the actual motion of the wheel; hence,
if the magnet be removed, there will still be electromagnetic in-
duction tending to maintain the current. Let us suppose the
velocity of the wheel to have been at first no greater than that
practically attained in ordinary experiments with Barlow's elec-
tromagnetic disk. As the magnet is gradually withdrawn let
the velocity be gradually increased so as to keep the strength of
the current constant, and, when the magnet is quite away, to
maintain the current solely by electromagnetic induction between
the fixed and moveable portions of the circuit. If, when the
magnet is away, the wheel be forced to rotate faster than the
limiting velocity of our previous supposition, the current will be
augmented according to the law of compound interest, and would
go on thus increasing without limit were it not that the resist-
ance of the circuit would become greater in virtue of the eleva-
tion of temperature produced by the current. The velocity of
rotation which gives by induction an electromotive force exactly
equal to that required to maintain the current, is clearly indepen-
dent of the strength of the current. The mathematical deter-
mination of it becomes complicated by the necessity of taking
into account the diffusion of the current through portions of the
disk not in the straight line between C and T; but it is very
simple and easy if we prevent this diffusion by cutting the wheel
into an infinite number of infinitely thin spokes, a great number
of which are to be simultaneously in contact with the fixed con-

ductor at **T**. The linear velocity of the circumference of the wheel in the limiting case bears to the velocity which measures, in absolute measure, the resistance of the circuit, a ratio (determinable by the solution of the mathematical problem) which depends on the proportions of the rectangle C T A B, and is independent of its absolute dimensions.

Lastly, suppose the wheel to be kept rotating at any constant velocity, whether above or below the velocity determined by the preceding considerations; and suppose the current to be temporarily excited in any way (for instance, by bringing a magnet into the neighbourhood and then withdrawing it); the strength of this current will diminish towards zero or will increase towards infinity, according as the velocity is below or above the critical velocity. The diminution or augmentation would follow the compound interest law if the resistance in the circuit remained constant. The conclusion presents us with this wonderful result: that if we commence with absolutely no electric current, and give the wheel any velocity of rotation exceeding the critical velocity, the electric equilibrium is unstable: an infinitesimal current in either direction would augment until, by heating the circuit, the electric resistance becomes increased to such an extent that the electromotive force of induction just suffices to keep the current constant.

It will be difficult, perhaps impossible, to realize this result in practice, because of the great velocity required, and the difficulty of maintaining good frictional contact at the circumference, without enormous friction, and consequently frictional generation of heat.

The electromagnetic augmentation and maintenance of a current discovered by Siemens, and put in practice by him, with the aid of soft iron, and proved by Maxwell to be theoretically possible without soft iron, suggested the subject of this communication to the author, and led him to endeavour to arrive at a similar result with only a single circuit, and no making and breaking of contacts; and it is only these characteristics that constitute the peculiarity of the arrangement which he now describes.

VII. *On Volta-Convection by Flame.*
By Sir William Thomson *LL.D., F.R.S.**

IN Nichol's Cyclopædia, article " Electricity, Atmospheric " (2nd edition), and in the Proceedings of the Royal Institution, May 1860 (Lecture on Atmospheric Electricity), the author

had pointed out that the effect of the flame of an insulated lamp is to reduce the lamp and other conducting material connected with it to the same potential as that of the air in the neighbourhood of the flame, and that the effect of a fine jet of water from an insulated vessel is to bring the vessel and other conducting material connected with it to the same potential as that of the air at the point where the jet breaks into drops. In a recent communication to the Royal Society " On a Self-acting Apparatus for Multiplying and Maintaining Electric Charges, with applications to illustrate the Voltaic Theory," an experiment was described in which a water-dropping apparatus was employed to prove the difference of potential in the air, in the neighbourhood of bright metallic surfaces of zinc and copper metallically connected with one another, which is to be expected from Volta's discovery of contact-electricity. In the present communication a similar experiment is described, in which the flame of a spirit-lamp is used instead of a jet of water breaking into drops.

A spirit-lamp is placed on an insulated stand connected with a very delicate electrometer. Copper and zinc cylinders, in metallic connexion with the metal case of the electrometer, are alternately held vertically in such a position that the flame burns nearly in the centre of the cylinder, which is open at both ends. If the electrometer-reading, with the copper cylinder surrounding the flame, is called zero, the reading observed with the zinc cylinder surrounding the flame indicates positive electrification of the insulated stand bearing the lamp.

It is to be remarked that the differential method here followed eliminates the ambiguity involved in what is meant by the potential of a conducting system composed partly of flame, partly of alcohol, and partly of metal.

In a merely illustrative experiment, which the author has already made, the amount of difference made by substituting the zinc cylinder for the copper cylinder round the flame was rather more than half the difference of potential maintained by a single
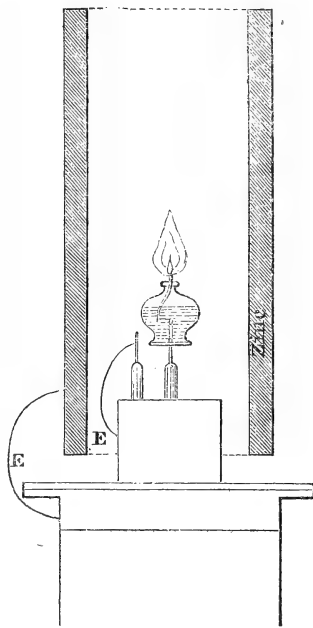
cell of Daniell's. Thus, when the sensibility of the quadrant divided-ring electrometer* was such that a single cell of Daniell's gave a deflection of 79 scale-divisions, the difference of the reading when the zinc cylinder was substituted for the copper cylinder round the insulated lamp was 39 scale-divisions. From other experiments on contact-electricity made seven years ago by the author, and agreeing with results which have been published by Hankel, it appears that the difference of potentials in the air in the neighbourhood of bright metallic surfaces of zinc and copper in metallic connexion with one another is about three-quarters of that of a single cell of Daniell's. It is quite certain that the difference produced in the metal connected with the insulated lamp would be exactly equal to the true contact difference of the metals, if the interior surfaces of the metal cylinders were perfectly metallic (free from oxidation or any other tarnishing, such as by sulphur, iodine, or any other body); provided the distance of the inner surface of the cylinder from the flame were everywhere sufficient to prevent conduction by heated air between them, and provided the length of the cylinder were infinite (or, practically, anything more than three or four times its diameter).

The author hopes before long to be able to publish a complete account of his old experiments on contact-electricity, of which a slight notice appeared in the Proceedings of the Literary and Philosophical Society of Manchester.

VIII. *On Electric Machines founded on Induction and Convection.* *By* Sir WILLIAM THOMSON, *LL.D., F.R.S.*†

TO facilitate the application of an instrument, which I have recently patented, for recording the signals of the Atlantic Cable, a small electric machine running easily enough to be driven by the wheelwork of an ordinary Morse instrument was desired; and I have therefore designed a combination of the electrophorus principle with the system of reciprocal induction explained in a recent communication to the Royal Society (Proceedings, June 1867), which may be briefly described as follows:—

A wheel of vulcanite, with a large number of pieces of metal (called carriers, for brevity) attached to its rim, is kept rotating rapidly round a fixed axis. The carriers are very lightly touched at opposite ends of a diameter by two fixed tangent springs. One of these springs (the earth-spring) is connected with the

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* See Proceedings of the Royal Society, June 20, 1867. [Phil. Mag. November 1867, p. 391.]

† Communicated by the Author.

earth, and the other (the receiver-spring) with an insulated
piece of metal called the receiver, which is analogous to the
" prime conductor " of an ordinary electric machine. The point
of contact of the earth-spring with the carriers is exposed to the
influence of an electrified body (generally an insulated piece of
metal) called the inductor. When this is negatively electrified,
each carrier comes away from contact with the earth-spring,
carrying positive electricity, which it gives up, through the re-
ceiver-spring, to the receiver. The receiver and inductor are
each hollowed out to a proper shape, and are properly placed to
surround, each as nearly as may be, the point of contact of the
corresponding spring.

The inductor, for the good working of the machine, should be
kept electrified to a constant potential. This is effected by an
adjunct called the replenisher, which may be applied to the main
wheel, but which, for a large instrument, ought to be worked by
a much smaller carrier-wheel, attached either to the same or to
another turning-shaft.

The replenisher consists chiefly of two properly shaped pieces
of metal called inductors, which are fixed in the neighbourhood
of a carrier-wheel, such as that described above, and four fixed

Fig. 1.

Section.   Elevation.
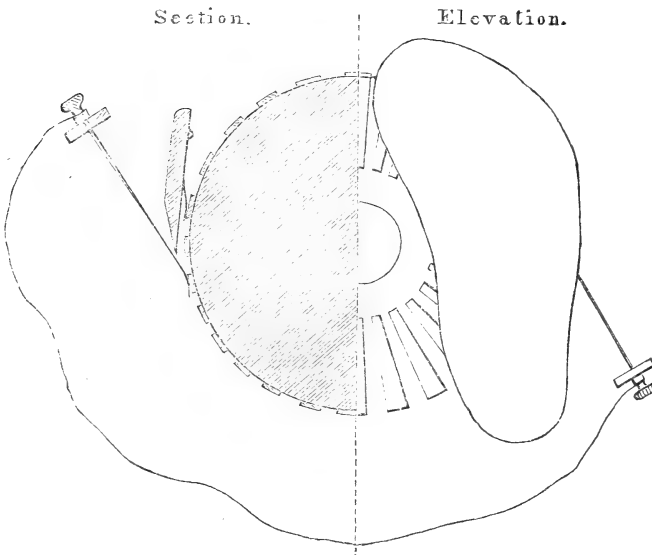
springs touching the carriers at the ends of two diameters. Two
of these springs (called receiver-springs) are connected respect-
F 2

ively with the inductors; and the other two (called connecting springs) are insulated and connected with one another (one of

Fig. 2.
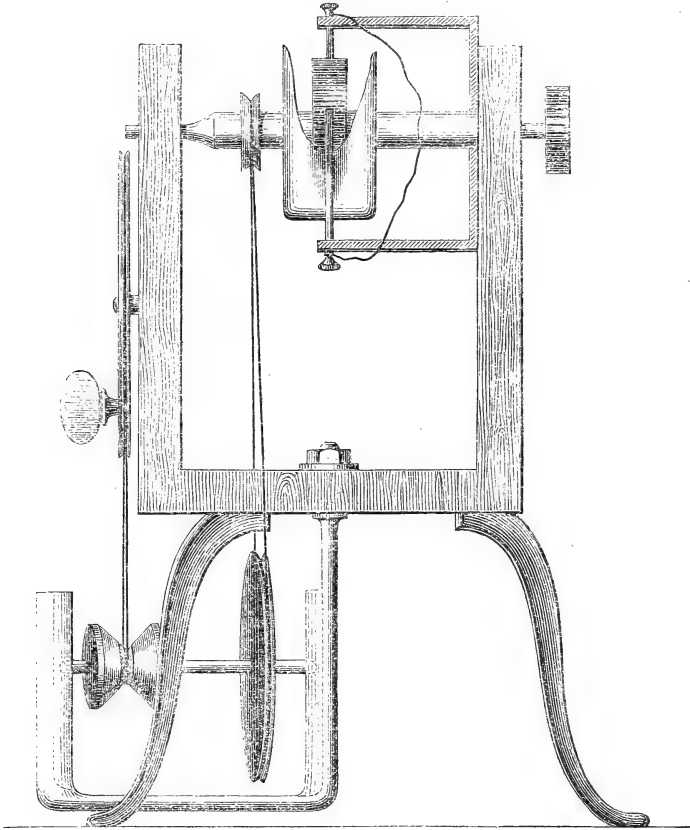
the inductors is generally connected with the earth, and the other insulated). They are so situated that they are touched by the carriers on emerging from the inductors, and shortly after the contacts with the receiver-springs. If any difference of potential between the inductors is given to begin with, the action of the carriers, as is easily seen, increases it according to the compound-interest law as long as the insulation is perfect. Practically, in a few seconds after the machine is started running, bright flashes and sparks begin to fly about in various parts of the apparatus, even although the inductors and connectors have been kept for days as carefully discharged as possible. Forty elements of a

dry pile (zinc, copper, paper), applied with one pole to one of the inductors, and the other for a moment to the connecting springs and the other inductor, may be used to determine, or to suddenly reverse, the character (vitreous or resinous) of the electrification of the insulated inductor. The only instrument yet made is a very small one (with carrier-wheel 2 inches in diameter), constructed for the Atlantic-Telegraph application; but its action has been so startlingly successful that good effect may be expected from larger machines on the same plan.

When this instrument is used to replenish the charge of the inductor in the constant electric machine, described above, one of its own inductors is connected with the earth, and the other with the inductor to be replenished. When accurate constancy is desired, a gauge-electroscope is applied to break and make contact between the connector-springs of the replenisher when the potential to be maintained rises above or falls below a certain limit.

Several useful applications of the replenisher for scientific observation were shown by the author at the recent Meeting of the British Association (Dundee),—among others, to keep up the charge in the Leyden jar for the divided-ring mirror-electrometer, especially when this instrument is used for recording atmospheric electricity. A small replenisher, attached to the instrument within the jar, is worked by a little milled head on the outside, a few turns of which will suffice to replenish the loss of twenty-four hours.

POSTSCRIPT, *Nov.* 23, 1867.

As has been stated, this machine was planned originally for recording the signals of the Atlantic Cable. The small " replenisher " represented in the diagrams has proved perfectly suitable for this purpose. The first experiments on the method for recording signals which I recently patented were made more than a year ago by aid of an ordinary plate-glass machine worked by hand. This day the small " replenisher " has been connected with the wheelwork drawing the Morse paper on which signals are recorded, and, with only the ordinary driving-weight as moving power, has proved quite successful.

The scientific applications indicated when the communication was made to the British Association have been tested within the last few weeks, and especially today, with the assistance of Professor Tait. The small replenisher is now made as part of each quadrant electrometer. It is permanently placed in the interior of the glass Leyden jar; and a few turns by the finger applied to a milled head on the outside of the lid are found sufficient to replenish the loss of twenty-four hours. A small instrument has also

been made and tested for putting in practice the plan of equal-
izing potentials, described verbally in the communication to the
British Association, which consisted in a mechanical arrangement
to produce effects of the same character as those of the water-
dropping system, described several years ago at the Royal Insti-
tution*. The instrument is represented in the annexed sketch
(fig. 3). A T and A'T' are two springs touching a circular row of

Fig. 3.
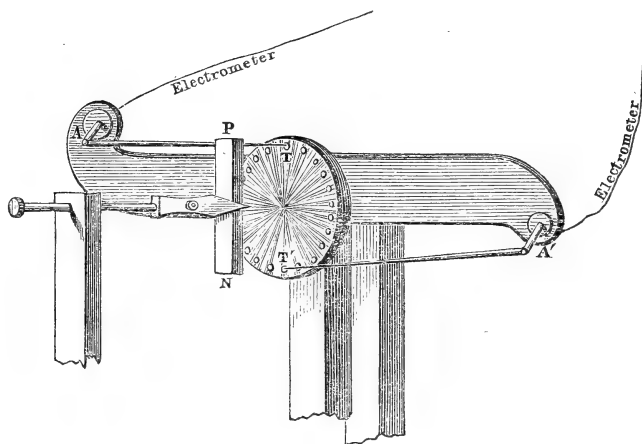
small brass pegs† insulated from one another in a vulcanite disk.
These springs are insulated, one or both, and are connected with
the two electrodes of the electrometer—or one of them with the
insulated part of the electrometer, and the other with the metal
enclosing the case, when there is only one insulated electrode.
One application is to test the " pyro-electricity " of crystals;
thus a crystal of tourmaline, P N, by means of a metal arm holding
its middle, is supported symmetrically with reference to the disk
in a position parallel to the line T T', and joining the lines of con-
tact of the springs. When warmed (as is conveniently done by

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* Lecture on Atmospheric Electricity, Proceedings of the Royal Insti-
tution, May 1860. See also Nichol's Cyclopædia, article " Electricity,
Atmospheric."

† [I now find a smaller number of larger disks to be preferable, as consi-
derable disturbances are produced by the numerous breakings of contact,
unless the two springs are in precisely the same condition as to quality and
cleanness of metal surface. Thin stiff platinum pins attached to the disks,
and very fine platinum springs touching them as they pass, will probably
give good and steady results if the springs are kept very clean. The small-
est quantity of the paraffin (with which, as usual in electric instruments,
the vulcanite is coated), if getting on either spring, would probably produce
immense disturbance.—December 23, 1867.]

a metal plate at a considerable distance from it), it gives by ordinary tests, as is well known, indications of positive electrification towards the one end P, and of negative electrification towards the other end N. The wheel in the arrangement now described is kept turning at a rapid rate; and the effect of the carrier is to produce in the springs T A, T' A' the same potentials, approximately, as those which would exist in the air at the points T, T' if the wheel and springs were removed. The springs being connected with the electrodes of the divided-ring quadrant electrometer, the spot of light is deflected to the right, let us say. After continuing the application of heat for some time the hot plate is removed, and a little later the spot of light goes to zero and passes to the left, remaining there for a long time, and indicating a difference of potentials between the springs, in the direction A' T' positive and A T negative. The electrometer being of such sensibility as to give a deflection of about 100 scale-divisions to the right or left when tested by a single galvanic cell, and having a range of 300 scale-divisions on each side, it is necessary to place the tourmaline at a distance of several inches from the disk to keep the amount of the deflection within the limits of the scale.

Another application of this instrument is for the experimental investigation of the voltaic theory, acording to the general principle described in the communication to the Royal Society already referred to*. In it two inductors are placed as represented in fig. 4. The inner surface of each of these is of smooth

Fig. 4.
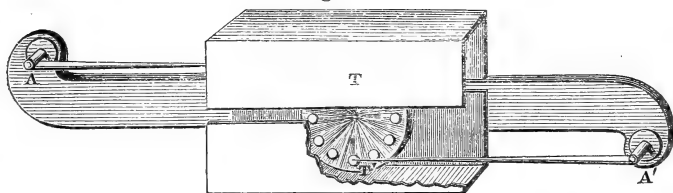
brass; and one of them is lined wholly, or partially, with sheet zinc, copper, silver, or other metal to be tested. Thus, to experiment upon the contact difference of potentials between zinc and copper, one of the inductors is wholly lined with sheet zinc or with sheet copper, and the two inductors are placed in metallic communication with one another. The springs are each in metallic communication with the electrodes of the quadrant mirror electrometer, and the wheel is kept turning. The spot of light is observed to take positions differing, according as the lining is zinc or copper, by $72\frac{1}{2}$ per cent. of the difference pro-

* Proceedings of the Royal Society, May 1867.

duced by disconnecting the two inductors from one another and connecting them with the two plates of a single Daniell's cell, when either the zinc or the copper lining is left in one of them. These differences are very approximately in simple proportion to the differences of potentials between the pairs of the opposite quadrants of the electrometer in the different cases. The difference between the effects of zinc and of copper in this arrangement is of course in the direction corresponding to the positive electrification of the quadrants connected with the spring whose point of contact is exposed to the zinc-lined inducing surface. It must be remembered, however, as is to be expected from Hankel's observations, that the difference measured will be much affected by a slight degree of tarnishing by oxidation, or otherwise, of the inner surface of either inductor. When the copper surface is brought to a slate-colour by oxidation under the influence of heat, the contact difference between it and polished zinc amounts sometimes, as I found in experiments made seven years ago, to 125, that of a single cell of Daniell's being called 100.

A useful application of the little instrument represented in fig. 4 is for testing insulation of insulated conductors of small capacity, as, for instance, short lengths (2 or 3 feet) of submarine cable, when the electrometer used is such that its direct application to the conductor to be tested would produce a sensible disturbance in its charge, whether through the capacity of the electrometer being too great, or from inductive effects due to motion of the moveable part, or parts, especially if the electrometer is "heterostatic"*. In this application one of the inductors is kept in connexion with a metal plate in the water surrounding the specimen of cable to be tested; and the other is connected with the specimen, or is successively connected with the different specimens under examination. The springs are connected with the two electrodes of the electrometer as usual. The small constant capacity of the insulated inductor, and the practically perfect insulation which may with ease be secured for the single glass or vulcanite stem bearing it, are such that the application of the testing apparatus to the body to be tested produces either no sensible change, or a small change which can be easily allowed for. It will be seen that the small metal pegs carried away by the turning-wheel from the point of the insulated spring, in the arrangement last described, correspond precisely to the drops of water breaking away from the nozzle in the water-dropping collector for atmospheric electricity.

A form bearing the same relation to that represented in the

* Lecture on Atmospheric Electricity (Proceedings of the Royal Institution, 1860).

drawings that a glass-cylinder electric machine bears to a plate-glass machine of the ordinary kind will be more easily made, and will probably be found preferable, when the dimensions are not so great as to render it cumbrous. In it, it is proposed to make the carrier-wheel nearly after the pattern of a mouse-mill, with disks of vulcanite instead of wood for its ends. The inductor and receiver of the rotatory electrophorus machine, or the two inductor-receivers of the replenisher, may, when this pattern is adopted, be mere tangent planes; but it will probably be found better to bend them somewhat to a curved cylindrical shape not differing very much from tangent planes. When, however, great intensity is desired, the best pattern will probably be had by substituting for the carrier-wheel an endless rope ladder, as it were, with cross bars of metal and longitudinal cords of silk or other flexible insulating material. This, by an action analogous to that of the chain-pump, will be made to move with great rapidity, carrying electricity from a properly placed inductor to a properly shaped and properly placed receiver at a distance from the inductor which may be as much as several feet.

IX. *Notices respecting New Books.*

Sound. A Course of Eight Lectures delivered at the Royal Institution of Great Britain. By JOHN TYNDALL, *LL.D., F.R.S.* London: Longmans and Co. 1867. (8vo, pp. xiii and 335.)

WE hardly think that this work—excellent though it is in many ways—will be entirely satisfactory to serious students of science. To the reader who has once acquired a taste for the intellectual pleasure which comes with real scientific knowledge, the simple, unadorned, and unimpassioned style which aims at nothing but clearness and accuracy, and which ordinary readers are apt to find so dull and cold, is commonly far the most acceptable. The true lover of science cares more to be told exactly what the phenomena of nature are, and what are the conditions whereon their recurrence depends, than for even the most eloquent and poetical descriptions of their beauty. He is conscious that if he can only know them, their beauty will be evident enough. Nor does it move him greatly when he is called upon to marvel at the *wonders* of science. Nothing would astonish him so much as to find that the Truth of Nature was really like what in his ignorance he fancied it, or was in fact anything else than wonderful.

But Professor Tyndall does not address exclusively or even principally those whose interest in science is already awakened. He says that in this work he has " tried to render the science of acoustics interesting to all intelligent persons, including those who do not possess any special scientific culture." This sentence, we think, justifies, as the titlepage explains, the presence in this book of a

good deal that would be out of place if it occurred in a work intended as a text-book for scientific students. Doubtless many "intelligent persons" listened to these lectures at the Royal Institution, and many more will read them in their present form, with pleasure and profit, who would never have exerted their intelligence for ten minutes in trying to read a more systematic or (as they would probably call it) dry treatise on acoustics. Such a result is one for which Professor Tyndall deserves the thanks, not only of the "intelligent persons" aforesaid, but also of those who have made science the occupation of their lives. The nature of the service rendered to this latter class by works like the present was so well stated a few months ago at Dundee by Sir William Thomson, while speaking of the author's previous work on "Heat," that we cannot do better than quote his words :—" The scientific world are much indebted to Dr. Tyndall, not merely for his investigations, but for the manner in which he has attracted interest to the results of science, and for the beautifully clear explanations he has given of scientific principles. Scientific men are extremely dependent on the sympathy of the rest of the world ; and this is very largely increased when the illustrations of scientific investigations are made known in a clear and interesting manner, as Dr. Tyndall has made them known, to a very large part of the population of this country and throughout the civilized world." This recognition of the value to science of Dr. Tyndall's literary labours is in our opinion extremely well deserved, and is as applicable to the work before us as to that to which it originally had reference. Nevertheless it is certain that the interest excited by the magnificent experiments which he exhibits so admirably to his audience at the Royal Institution, and which he describes with such vivacity and graphic power that those who only read of them must feel almost as if they saw them performed, is by no means a sure sign that those who feel it have any deep sympathy with science for its own sake. These experiments are often of such a kind that the least intelligent person, looking upon them merely as beautiful sights, and without any perception of their scientific significance, could not witness them without delight ; but they are to the general truths and reasonings which constitute the real framework of science what the sweetmeats and playthings of childhood are to the solid food and serious occupations of manhood. By this we do not at all mean to imply that the fare which Professor Tyndall offers consists solely of sweetmeats, but simply to warn any who may be inclined to pick out these, and to leave the more substantial food to which they are only intended to impart a flavour, that they must not expect to derive from them any great amount of scientific nourishment.

The first of the eight lectures contained in this volume treats of the nature of sound, its production, the conditions which determine its greater or less intensity, and the mechanism and velocity of its propagation in air and other media. The effect which the changes of temperature caused by the compression and expansion of air have in increasing the velocity of sound is dwelt upon in this lecture at considerable length, and explained with admirable clearness.

The principal subjects discussed in the second lecture are the physical difference between noises and musical sounds, the nature of musical pitch, the connexion between the pitch and wave-length of musical sounds, and the limits of pitch within which sounds are audible and available for musical purposes.

The whole of the third lecture is devoted to the explanation of the laws of vibrating strings. Some beautiful experiments in illustration of this subject, which were made known a few years ago by Professor Melde of Marburg, have been extended by Professor Tyndall with wonderful ingenuity, so that he is able in this lecture to render strikingly *visible* the separate effect of each of the conditions upon which the rate of vibration of a stretched string depends. For their combination of intrinsic beauty with demonstrative value, the experiments described in this lecture are perhaps on the whole the most remarkable in the book; and the verbal explanations of the phenomena they are intended to illustrate are not less excellent. The production of stationary vibrations, by the combined action of direct and reflected progressive waves, however, is a subject which, considering its importance, might with advantage have been discussed rather more fully.

The fourth lecture treats of the transverse vibrations of rods and plates; but, though full of excellent matter, it presents less of novelty, either in the way of experiment or of exposition, than most of the others. An accidental transposition on page 151 produces a misstatement: the number of vibrations of a bell in a given time is said to vary "directly as the square of the thickness, and inversely as the bell's diameter," instead of directly as the thickness, and inversely as the square of the bell's diameter.

The fifth lecture is taken up with the laws of the longitudinal vibrations, first of solid bodies, and then of air and gases, naturally including the theory of organ-pipes and indirect methods of measuring the velocity of sound. A little misconception may, we think, possibly arise with regard to the nature of longitudinal vibrations if they are spoken of, as is the case several times in this lecture, as "running to and fro." Although they take place lengthwise, they are of course as stationary and unprogressive as transverse vibrations. The results of Helmholtz's researches into the nature of the vowel-sounds, and Kundt's method of comparing the relative velocities of sound in air and in solid bodies, are very lucidly explained in this lecture for the first time, so far as we know, in an English elementary work.

From the consideration of the vibrations of air in organ-pipes, it is an easy transition to the examination of the similar vibrations produced in the air contained in a glass tube by a burning gas-jet, and thence to the investigation of the effects of sonorous vibrations on naked gas-flames, jets of unignited gas, and of water. These subjects, which Professor Tyndall has made peculiarly his own, occupy the sixth lecture. As an example of the striking experiments here described, and as a specimen of the graphic style of the lecturer, we may quote a passage from this lecture (pp. 240–241):—

" The most marvellous flame hitherto discovered is now before
you. It issues from the single orifice of a steatite burner, and reaches
a height of 24 inches. The slightest tap on a distant anvil reduces
its height to 7 inches. When I shake this bunch of keys the flame
is violently agitated and emits a loud roar. The dropping of a six-
pence into a hand already containing coin, at a distance of 20 yards,
knocks the flame down. I cannot walk across the floor without
agitating the flame. The creaking of my boots sets it in violent
commotion. The crumpling or tearing of a bit of paper, or the
rustle of a silk dress, does the same. It is startled by the patter of
a raindrop. I hold a watch near the flame, nobody hears its ticks;
but you all see their effect upon the flame. At every tick it falls.
The winding up of the watch also produces tumult. The twitter of
a distant sparrow shakes the flame down; the note of a cricket
would do the same. From a distance of 30 yards I have chirruped
to this flame and caused it to fall and roar. I repeat a passage from
Spenser :—

> ' Her ivory forehead, full of bounty brave,
>   Like a broad table did itself dispread
> For love his lofty triumphs to engrave
>   And write the battles of his great godhead.
> All truth and goodness might therein be read,
>   For there their dwelling was; and when she spake,
> Sweet words, like dropping honey, she did shed;
>   And through the pearls and rubies softly brake
> A silver sound, which heavenly music seemed to make.'

" The flame picks out certain sounds from my utterance ; it notices
some by the slightest nod, to others it bows more distinctly, to some
its obeisance is very profound, while to many sounds it turns an en-
tirely deaf ear."

The seventh lecture treats of the phenomena which result from
the coexistence of two or more sets of vibrations in the same me-
dium, namely interferences, beats, and resultant tones.

In the eighth lecture the principles previously explained are ap-
plied to elucidate the physical causes of harmony and discord, and
the distinctive characteristics of the principal musical intervals.
Professor Tyndall of course adopts Helmholtz's view that rapid beats
are the cause of discord, and that resultant tones are an independent
phenomenon; but his explanation of the different effects upon the
ear of resultant tones and of beats is not quite accurate. In order
to account for the disturbing effects of the latter as compared with
the perfect musical character of the former, we are told (p. 299) that
whereas " the impulses of ordinary sonorous waves are gently gra-
duated, in the beats, on the contrary, the boundaries of sound and
silence are abrupt, and they therefore subject the ear to that jerking
intermittence which expresses itself to consciousness as dissonance."
Very little reflection upon the way in which beats are generated, or
a glance at figure 145 (p. 269), is sufficient to show that the sudden
alternations of sound and silence here spoken of do not exist. The

real cause of the disagreeable effect of beats upon the ear is no doubt that suggested by Helmholtz when he compares it to the unpleasant effect produced on the eye by frequent alternations of light and darkness. Resultant tones, on the other hand, are probably perceived, just as though they were primary tones, through the agency of quite a distinct set of ear-fibres (Corti's fibres) from those affected by the generating tones. In the same lecture (p. 301), speaking of the unsatisfactory musical character of simple tones, such as the tones of tuning-forks or of stopped-diapason organ-pipes, Professor Tyndall contents himself with saying that such tones " would be like pure water, flat and dull, ... and would not satisfy the demand of the ear for brightness and energy." The reason of this—namely that, with such tones, the difference between pure and impure intervals is revealed to the ear only by resultant tones, generally of the second or third order—is not alluded to. On pages 305 and 306 Professor Tyndall has reproduced Helmholtz's diagrams showing the relative degrees of consonance and dissonance resulting from the combination of the tone middle *c* with every possible tone up to treble *c*, and of the latter with every tone up to *c* in alto. In the explanation of these diagrams, it should have been stated, not only that the marks *es* and *as* " are the German names of a flat third and flat sixth," but also that *b* stands for a flat seventh, our *b* ♭ and *b* ♮ being respectively represented in German musical notation by *b* and *h*.

The value of the book for educational purposes is much increased by a short summary, following each lecture, of the most important facts or principles that have been stated in it. But for easy reference to particular points it requires a greatly improved index.

Professor Tyndall has in this work introduced several terms which are new to the English vocabulary of acoustics. *Overtones* and *resultant tones* are, we think, excellent English equivalents for the German *Obertöne* and *Combinationstöne*, and we receive them gratefully. We cannot, however, say as much for *clangtint* as English for *Klangfarbe*. Our objections to this term are several. In the first place, it appears to us unnecessary, the word *quality* having already a perfectly well-understood technical meaning coincident with that of the proposed new word. Secondly, the German word *Klangfarbe* is itself objectionable, being founded upon a false analogy, the property of sound which corresponds to the colour of light being pitch and not quality. Lastly, *Klang* in German is used for sounds of all kinds, and cannot be correctly translated by *clang*, which already implies a special quality in the sound to which it is applied. To speak of the clang of a flute, for instance, is almost a *contradictio in adjecto*.

X. *Intelligence and Miscellaneous Articles.*

ON A NEW PHOTOMETER.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,   Melton, December 16, 1867.

I REGRET to find that I have stated $\frac{1}{60}$ inch as the size of the diaphragm *y*, it should be $\frac{1}{6}$ inch : this is not your printer's fault, but *my own.*

Perhaps the limit of darkness at which a thing can be seen varies in different people, so that the observer must to some extent determine for himself the size of the diaphragms. Instead of the microphotograph, I now prefer *tissue paper at x*, and a strong convex lens at its principal focus behind *x* in B. A transparent glass picture varying in depth of shade lies between the lens and the microscope A.

With many apologies for the space I have taken,

I am, Gentlemen,

Your obedient Servant,

C. H. BENNINGTON.

NEW OBSERVATIONS ON THE SPECTRA OF THE FIXED STARS.
BY FATHER SECCHI.

In some previous communications I have shown that the spectra of the fixed stars may be referred to three characteristic types, represented (1) by *a* Lyræ (Vega), (2) by *a* Herculis, and (3) by *a* Bootæ (Arcturus), or by our sun itself. Between the first and the last category nearly all the stars already investigated are pretty equally divided.

These results deserved to be confirmed by more comprehensive and more numerous observations; and these I have made. Upwards of 500 stars, the largest in the heavens, have been examined from the Observatory of the Collegio Romano; and I have given a complete description of more than 400 of them.

The details of this investigation are not less interesting. The first type, *a* Lyræ, contains in fundamental lines two very distinct hydrogen rays—that, namely, in the blue which coincides with the solar line *f*, and one in the violet, which, as far as I can conclude from M. Plücker's investigation of hydrogen, coincides with the line H γ. The line H α or C is seldom visible ; for the red is either absent in this type, or is at any rate very feeble.

M. Plücker has shown that the hydrogen lines H β and H γ are broader at higher temperatures (and that the lines in question are present in these stars is indicated by their breadth), and that the one in the violet is always broader than that in the greenish blue. In some stars these lines are somewhat diffused, which M. Plücker has also found to be the case with hydrogen lines when the temperatures and pressures are considerable.

It thus appears that hydrogen is the chief constituent of the stars of this group. The peculiar phenomena in γ Cassiopeia, where, instead of the dark line *f*, there is a bright one, might be explained by the fact that hydrogen gives at low temperatures a continuous spectrum in which the line *f* is bright, and that hydrogen, when present in small quantity, does not invert the spectrum. There are doubtless other lines between those of hydrogen, but they are relatively very feeble; the most prominent are those of magnesium and of sodium. The second type, that of α Herculis, is far less numerous, but is remarkably constant. Direct measurements gave exactly the same lines in the same places in all stars of this type. The only difference is in the circumstance that in the normal stars α Herculis, β Pegasi, *o* Ceti, ρ Persei, the lines which separate the columns are quite sharp and dark; while in some, as in α Orionis and α Scorpionis, they occur, though rather weak, in the less-refrangible part of the spectrum. This peculiarity might be thought to indicate a difference which in fact does not exist.

It is curious that this type embraces the strongly red-coloured and the variable stars. The star *o* Ceti (Mira) is a remarkable proof of this; I observed it last September, but its smallness did not justify any conclusions. In March it was of the fourth and fifth magnitudes; it exhibited the colonnade of α Herculis with surprising accuracy; its feebleness, however, caused its spectrum to appear shorter, and the outside lines to lie closer. The red star of Auriga (Lalande 12561) (right ascension 6^h 27^m, declination 38° 33') belongs also to this type; only the second and third columns coalesce, as well as also the fourth and fifth. It is indeed surprising to observe such identity in the spectra of various stars. I imagine that the stars belonging to this type are tolerably numerous; but their colour is so dark that their characters cannot be determined.

The third type, that of the sun, would seem from its nature to present a great number of differences; yet this is not the case. The chief differences are that there are fine lines in more or less compact groups; but these lines have the same position, which is not that of the previous type. The magnesium line, which is very much developed in the third type, does not show the same union of adjacent lines as in the second type; moreover in the third type the line *f* can always be readily distinguished, while it is wanting in the second. Owing to these differences it is easy to discriminate this type from the others, even if the lines are so grouped that they appear similar to it. The doubtful cases which I have met with may be resolved by subsequent measurements undertaken at leisure.

Certain types are peculiar to certain regions of the heavens, even when the number of stars is tolerably large. The type Orion characterizes one portion of the image of the Dog and the Hare, but is scarce in other parts of the heavens; green predominates in these stars, which is characteristic of the nebulæ. The yellow stars, which belong to the third type, are very numerous in the Whale and in Eridanus. The Ox is formed exclusively of stars of the first type, Aldebaran and some others excepted.

The following Table gives the position of the chief lines in the spectra of these three types of stars, compared with that of our sun; and this can be done with the same instrument for Venus and Mars. One turn of the micrometer $=2·71$.

Position of the chief lines in the Spectra of the Planets and Fixed Stars.

In parts of the micrometer.

Venus.	Mars.	α Herculis.	β Pegasi.	α Orionis.	Arcturus.	Mira Ceti	Vega.	α Persei.
r								
A =1·72	......	......	......	1·98				
B =2·16	......	......	......		2·13			
C =2·50	......	a'=2·48	2·57	2·64				
D*=3·22	3·24	a =3·25	3·22	3·22	3·38	3·18	3·12	
δ =3·51	......	b =3·86	3·83	......	......	3·19	3·62	
E =4·83	......	c =4·24	4·19	4·15	4·77	4·31	......	4·86
b† =5·09	5·14	d =5·11	5·11	5·11	5·09	5·11		
X =5·62	......	e =5·95	5·99	5·95	5·95			
F =6·27	6·35	f =6·81	6·85	6·78	6·21	6·77	6·28	6·30
G =7·98	8·01	g =7·64	7·68	7·49	7·98	8·15		
H =9·40	9·64	......	......	8·43	9·65		9·15	8·29
W =	......	......	......	......	......	11·03		

From this Table an identity is manifest, as accurately as can be proved by a comparison of the fundamental lines, between the various red-coloured stars, and between the yellow stars and our sun. The Table also shows the difference in the position of the lines in the white stars of the type of Vega.

It is curious that red stars of the seventh magnitude, like Lalande 12561, give a measurable spectrum, while this is not the case with white stars of the same magnitude. This arises from the feeble dispersion of their light, by which separate bright lines are formed pretty much as in the nebulæ. A light which is not dispersed, though it be feeble, retains a remarkable intensity. Thus I could distinctly see the separate sodium lines in the flame of an ordinary small candle at a distance of 2 kilometres.

It is to be remarked that in the red stars the dark lines are really bands like those which the absorption of our atmosphere produces in solar light. Thus the line D is enormously broadened, far more than the very fine sodium line. This proves that these stars are surrounded by very absorbent atmospheres, the nature of which cannot be made out until chemists can distinguish what belongs in the spectrum *to the nature* of the substance from what depends on the *temperature.*—*Comptes Rendus*, vol. lxiv. p. 774.

* Sodium.   † Magnesium.

XI. *On certain Thermomolecular Relations of Liquids and their Saturated Vapours.* By JOHN JAMES WATERSTON, *Esq.*

[With Four Plates.]

To the Editors of the Philosophical Magazine and Journal.

1 Ardross Street, Inverness,
GENTLEMEN,   August 13, 1867.

§ 1. IN the *Annales de Chimie* for May 1859 there is an account of some experimental researches on the dilatability of volatile liquids by M. Drion; and in the Philosophical Magazine for May 1864 I have shown, by a graphical analysis of M. Drion's results, that they indicate, as a general law of liquid expansion, that the inverse of the *absolute* increment of volume diminishes regularly as the temperature ascends. For example, if a liquid expands $\frac{1}{1000}$ at 0°, and $\frac{1}{950}$ at 10° per 1° rise of temperature, it will be found that at 20° the expansion is $\frac{1}{900}$, at 30° it is $\frac{1}{850}$, at 40° it is $\frac{1}{800}$, and so on to 200°, where the rate would be $\frac{1}{0}$, considered purely as a mathematical law. The unit is taken as the volume at a certain fixed temperature, say 0° C. Thus in the above example the expansion of $\frac{1}{800}$ at 40°, and $\frac{1}{750}$ per 1° at 50° means the $\frac{1}{800}$ and $\frac{1}{750}$ of the volume it had at 0°, *not* the $\frac{1}{800}$ and $\frac{1}{750}$ of the volume at the respective temperatures 40° and 50°. The first is the *absolute* increment, and the second is the *relative* increment. M. Drion's observations on muriatic ether and sulphurous acid were so regular that it was distinctly brought out by them that the law has

reference to the absolute increment of volume, not to the relative increment, as I had at first deduced from my own observations in sealed tubes at high temperatures.

§ 2. This was a fortunate discovery, because, on extending the inquiry to the numerous chemically pure liquids experimented upon by M. Pierre*, other relations make their appearance that confirm the general law, and further develope an interesting connexion between molecular volume, liquid cohesion, and saturated vapour-density, which we are enabled to trace distinctly by means of M. Regnault's great and admirable labours published in the twenty-first and twenty-sixth volumes of the Memoirs of the French Academy.

§ 3. Although a good deal of labour is required to bring out the numerical results from the observations, the thermomolecular relations are simple enough in their nature. I will endeavour to explain them concisely by diagram before proceeding to give the evidence upon which they are founded, and for simplicity will confine the attention to two liquids chemically analogous,—the hydrobromic and hydriodic ethers.

In fig. 1 the lines n A B G, $n\,a\,b$ G′, that represent both the saturated-vapour density and the liquid expansion of these bodies,

Fig. 1.
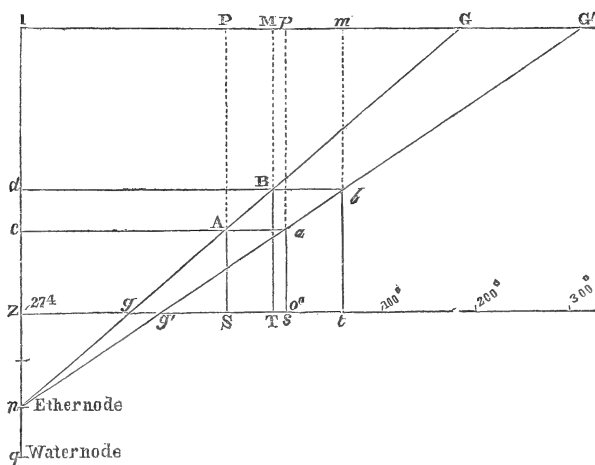
are obtained from M. Regnault's observations of pressure under the boiling-point (those taken by the dynamic method are preferred). A temperatare t, reckoned from $-274°$, the zero of gaseous tension, is represented by z S, and S A is the *sixth root*

* *Annales de Chimie et de Physique,* vols. xv., xix., xx., xxi., xxxi.

of the quotient of the corresponding pressure by z S.   The other observations of pressure (under the boiling-point) of hydrobromic ether treated in the same way give points which lie in a straight line A B.   Similarly the pressure-observations of hydriodic ether give points which lie in a straight line $a\,b$; and these lines produced *meet at* n, which is in the line $n\,z\,l$, a perpendicular to z S (the axis of temperature) passing through z.

§ 4. In a chart thus constructed, the pressure corresponding to a given point B is equal to the sixth power of B T (the ordinate of that point) multiplied by z T its abscissa, and, comparing two points B and b equidistant from the axis, the density is the same at each if the vaporous body is the same; or the number of molecules in a volume is the same if the vaporous body is different.   Hence if, in two lines A B, $a\,b$, points are taken equidistant from z T, the *volume* of a molecule at one is equal to the volume of a molecule at the other.

It is also evident, since the lines meet at $-274°$, that the temperatures of those points, reckoning from z, are in a constant ratio; *e. g.*, A a being parallel to B b, we have

$$c\mathrm{A} : c\,a = a\mathrm{B} : d\,b = l\mathrm{G} : l\mathrm{G}' = \tan \angle \mathrm{G}nl : \tan \angle \mathrm{G}'nl = 159 : 177,$$

which are the numerical values of the tangents for these ethers. They are denoted generally by the symbol h.

§ 5. This ratio also dominates over the volumes of the *liquid* molecules at these respective temperatures; *e. g.* the liquid volume of a molecule of the hydrobromic ether at B (being the quotient of its vapour-density by the specific gravity of the liquid at that temperature, and represented by the symbol μ) is to the liquid volume of a molecule of the hydriodic ether at b as dB to $db = 159 : 177$.

§ 6. It has now to be explained how these lines represent the expansion of the respective liquids throughout their range of temperature.

Suppose we had complete Tables of the expansion of these two liquids, the first having reference to a volume considered as a unit at A, and the second having reference to a volume considered as unity at a; also let the volumes for each degree in the case of the first liquid be given, and in the second the volumes for each $\frac{177}{159}$ degree be given.   The Tables will be found to be *identical*; and computing the upper limit of temperature for each, it is found that, reckoned from $-274°$, they are in the ratio of $159 : 177 = h : h'$.

§ 7. It follows also that if $\dfrac{1}{\mathrm{PA}}$ represent the rate of expansion per degree at A, $\dfrac{1}{\mathrm{MB}}$ is the rate at B, and $\dfrac{1}{pa} = \dfrac{1}{\mathrm{PA}}$ is also the

rate at a of the second liquid; but we have to keep in mind that the unit of volume, as well as the increment of temperature, is $\frac{177}{159}$ time the absolute value of the unit and increment of the first.

Thus the behaviour of the two liquids and their saturated vapours are precisely the same at absolute temperatures proportional to their liquid molecular volume.

The evidence is nearly complete that in the same category are to be found hydrochloric ether and chloroform.

§ 8. M. Regnault's researches on specific heat and latent heat enable us to advance another step.

The amount of heat-force (denoted by the symbol $C\omega$) required to vaporize *a molecule* of these ethers also follows the same ratio, $h : h'$. *E. g.* the amount of heat-force required to raise a liquid molecule of the first body, at B, to become a vapour molecule at the same temperature zT is to the amount required to raise a molecule of the second body, at b, from the liquid to the vapour condition at the temperature zt as $159 : 177$.

§ 9. The full meaning of this relation will be more clearly made out by referring to fig. 2, where the complete range of expansion of two liquids thus related is exhibited,—the ratio, however, being 1 to 2 instead of 159 to 177.

It is assumed that the law of expansion extends downwards to $-274°$ at A. At this zero we start with the molecular volume of one double that of the other $[A\,B = 2a\,b]$. In the axis of temperature take $AC = 2a\,c$, the corresponding molecular volumes are still in the ratio of 2 to 1; and this is the case all the way up to E, e, the points of transition, where the maximum volume, when liquid condition terminates, is nearly three times the initial volume at z computed from theory. From F and f draw $F\,\Delta'\,\Delta\,G, f\delta'\,\delta g$ parallel to axis. If $D\,\Delta$ is the value of $C\omega$ of the larger molecule at C, $D'\Delta'$ is the value of the same at C'; $d\,\delta$ is the value of $C\omega$ of the smaller molecule at c, and $d'\,\delta'$ the value of the same at c'.

The ratio of 2 to 1 is common to all these; $D\,\Delta = 2d\,\delta$, &c.; and the thermomolecular lines of these two liquids will be represented on fig. 1 if we suppose $n\,G$ to be drawn so that $lG = \frac{1}{2}\,lG'$.

The remarkable point to keep in view is that $C\omega$ and μ (molecular volume) follow the same ratio. The same *absolute* increment of μ is accompanied with the same *absolute* decrement of $C\omega$ at whatever part of the range it may be measured, either in the liquid with the small molecules, or in that with the large.

Take, for example, 300 cubic inches of muriatic ether at t temperature, and apply heat so that its volume may increase to 301, and let the quantity of heat absorbed or rendered latent be denoted by k. Take 30 cubic inches of the same liquid at temperature t, and apply heat so that its volume may increase to 31.

The quantity of heat absorbed or rendered latent is still k. Take 278 cubic inches of chloroform at temperature T, and

Fig. 2.
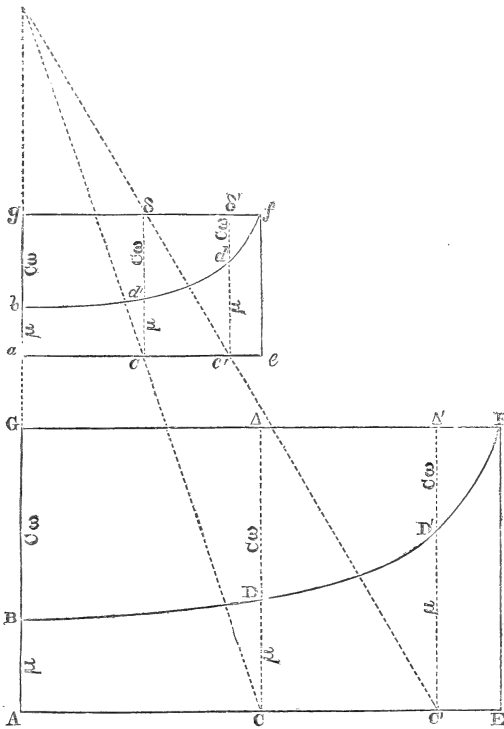
apply heat so that its volume may increase to 279, the quantity of heat absorbed is still k.

In another cluster of liquids the value of k is the same for each, but it is different from the k of the first set.

§ 10. The tangent of angle G $n l$ (fig. 1), termed h, is proportional to $C\omega$ generally in all liquids that possess n, the ethernode, when $C\omega$ is taken at absolute temperatures respectively proportional to h. Most of the bodies treated by Regnault have their vapour-lines directed to this point. Even mercury and sulphur exactly conform to it. We may thus infer that the vapour-lines of most of the bodies not experimented upon are also related to the same node, but not all.

§ 11. Water, whose vapour-line is very exactly determined by the different series of observations published in the twenty-first volume of the Memoirs, cuts $z n$ produced in q, and $z q = \frac{3}{2} z n$. To this point, called the water-node, converge the vapour-line

of pyroxylic spirit and methoxylic ether; there is also evidence that other bodies of a special character belong to it.

§ 12. There are sixteen bodies, chemically pure, whose lines of expansion, as well as of saturated vapour-density, have been determined. In nine the upper limiting temperature (G), derived from the expansion-observations being laid off on the vapour-line, are found to range parallel to the axis of temperature. In three of the sixteen the observations are confined to too small a range and are too irregular to give G with certainty; but the average of several trials makes it likely that they also conform. Of the remaining four, mercury has its upper limit four times as far removed from the axis as the preceding.

§ 13. The line of alcohol-vapour does not trend to either node; it is specially related to the line of water-vapour by crossing it near where it meets the axis. At this point also the lines of sulphuric-acid vapour and hydrates intersect; hydrated alcohol also. These are the only cases of such axial relation yet developed. The position of the upper limit of expansion of these bodies has not yet been determined.

§ 14. It is remarkable that $z\,l$ (fig. 1) is just three times $z\,n$. What recondite principle determines this ratio of 1 to 3? Why is the vapour-line determined by the sixth root of density? Space has *three* rectangular *dimensions* and *six* rectangular *directions*; and these ratios continually make their appearance in the dynamical theory of gases, in consequence of the relation of space to *resolved forces*. It is natural to think that this is the parent of the triad in both cases.

§ 15. Another relation, differing from the above, is exemplified in two analogous chlorides. The vapour-line of the trichloride of phosphorus, $Cl^{1\frac{1}{2}}\,P^{\frac{1}{4}}$ (boiling-point 74°), trends to the ether-node (Plate III.). If the vapour-line of the trichloride of arsenic, $Cl^{1\frac{1}{2}}\,As^{\frac{1}{4}}$ (boiling-point 134°), trends to the same, we have two lines related as those in fig. 1; but the volume of the liquid molecule of one measured at A is *equal* to that of the other measured at a instead of being as $h : h'$.

Evidence of the Law of Saturated-vapour Density.

§ 16. The law has reference to density, not pressure, and does not appear subject to deviation. To obtain density from pressure we have to divide the pressure by the temperature reckoned from the zero of gaseous tension, $-274°$; that is, in cases where the deviation from the laws of Mariotte, Dalton, and Gay-Lussac is too small to be noticed, as it is assumed to be in Regnault's observations of pressure under the boiling-point. Each observed pressure in millims. was divided by its tempera-

ture reckoned from $-274°$; the sixth root of the quotient was computed and laid off by scale as ordinate to the temperature: *e. g.* steam at $100°$, pressure 760 millims., $\left\{\dfrac{760}{374}\right\}^{\frac{1}{6}} = 1\cdot 1254$ is the ordinate which in Plate I. is laid off to a scale of $13\frac{1}{3}$ inches to unity, the scale of temperature being 10 inches to $100°$.

§ 17. The straight line W A T E R passes through the points thus computed from the pressures at $30°$, $40°$, $50°$, $60°$, $70°$, and $100°$ of Regnault's *courbe graphique*. It is continued downwards in Plate II. to the axis of temperature, which it cuts at $-79°$. The chart-lines of equal pressure, from 10 to 1 millims., have been laid down, so that the divergence from the straight line may be properly estimated at the lower part of the range. The maximum divergence, it will be seen, does not exceed $\frac{1}{50}$ of an inch of mercury. This straight line produced downwards cuts the ordinate of $-274°$ in $1\cdot 226$.

§ 18. The next to examine is the line marked alcohol on Plate I. It will be remarked that the accordance is very complete. It is continued downwards in Plate II., and is found to cut the axis of temperature at $-82°\cdot 7$, being $3°\cdot 7$ lower than the water-line.

§ 19. There are nine sets of points in Plate II., marked $S^{\frac{1}{6}}O^{1\frac{1}{2}} + 18(HO^{\frac{1}{2}})$, &c., which are obtained from Regnault's observations of pressure of vapour from nine hydrates of sulphuric acid[*]. A straight line was drawn through each set, using a short straight edge; and this was *afterwards* produced downwards to cut the axis of temperature: thus was obtained an unbiased representation of the convergence of the lines as the means of estimating the probability of their cutting the axis at the same point as water. The boiling-point of the hydrate $S^{\frac{1}{6}}O^{1\frac{1}{2}}, 3(HO^{\frac{1}{2}})$ was found to correspond with the line drawn on the chart produced upwards to $171°$.

§ 20. The next step was to compute by simple proportion from the slope of each line the point where it intersects the ordinate at $-274°$. These were laid off and the lines drawn as shown in Plate III. The remarkable convergence towards one point at $-274°$, shown in this Plate, is thus a result quite unbiased by any anticipation. The computed value of $z\,n$ of the mercury-line is $0\cdot 803$, and of the sulphur-line $0\cdot 799$; the values for the other lines run between $0\cdot 776$ and $0\cdot 843$, except the sulphide-of-carbon. The water-line cuts it at $1\cdot 226$, two-thirds of which is $0\cdot 817$. This is where the lines of muriatic ether and sulphuric ether intersect, and is a fair average of the best of the others. The dynamic series of sulphurous acid point to the

[*] *Annales de Chimie et de Physique*, vol. xv. p. 174.

water-node, and the static series to the ether-node. The observations above 0°, both by Regnault and Faraday, point to the ether-node. The line of sulphide of carbon cuts the zero ordinate at 0·712. The points given by the observations on hydrochloric ether range in a regular curve; so they cannot strictly be held to conform; but the hydrobromic and hydriodic ethers give points very exactly in a line. The methyloxalic-ether points range pretty well in a line that is directed to the water-node. The pyroxylic-spirit points are not so exactly in range as the best of the others : two lines were drawn; the intersection of one is at 1·18, and of the other at 1·27; the mean is 1·225; so there is no doubt that its node is the same as that of water.

§ 21. It will be remarked (Plate I.) that above the boiling-point the observations decline below the straight line; this is quite consistent with the deviation from the law of Mariotte discovered by Regnault. The pressure is *less* than the density would give if that law were maintained at high pressures; and, *vice versâ*, the actual density is greater.

§ 22. I have only my own observations (made fifteen years ago) in sealed tubes to present as evidence of the law of density at high temperatures, and in a few cases up to the point of transition. The chart with the points of the original observations laid down will be found in the 'Archives' of the Royal Society for 1852, a copy of which is now before me; and it is gratifying to find that the line passing through the sulphuric-ether points (between 125° and 190°), produced downwards to meet the ordinate at − 274°, cuts it at 0·79, which, it will be admitted, is very close to the mean from Regnault's observations published in 1862. The tube observations were made, computed, projected on the chart, the line drawn through them, and the copy lodged in the Archives of the Royal Society ten years before the idea of such a nodal point existed. The line is placed, in Plate III., with the letter *w* across it. Its boiling-point was 41°, and spec. grav. 0·737 at 30° C., so it was not chemically pure. Seven graduated tubes filled in different proportions were simultaneously observed up to 190° C., this being five more than is mathematically required to obtain results for liquid volume and vapour-density from perfect observations, ample means were afforded to check the accuracy of their graduation, and of testing the identity of physical influences to which they were subjected during the observations. Four of them showed complete accordance.

§ 23. The second trial, with improved heater, was made with alcohol that had 19 per cent. water and boiled at 81°. Six tubes were employed, and the curves of liquid volume were established by repeated trials up to 216°. The accordance of all these

tubes throughout was satisfactory. The series of vapour-den-
sities derived from them led to the discovery of the law ; the
points are laid down on the chart in the Archives of the
Royal Society for 1852. The line produced downwards will
be found thereon to cut the axis of temperature at −79°, being
exactly the same as the line of water-vapour in Plate II. It is
marked off on Plate III.; and a cross mark at the upper end
denotes the point of transition found afterwards by another set
of observations in short tubes.

§ 24. Another specimen of dilute alcohol (62 per cent. water
and boiling-point 86°·5) was tried in four tubes up to 190°.
The points will be found in the same chart, and to range fairly
in a straight line that, when produced, cuts the axis at −73°.

§ 25. A specimen of sulphide of carbon that boiled at 49° was
tried up to 160°; the points and line drawn through them are
also to be found on the chart. It is curious that the line pro-
duced downwards cuts the zero ordinate at 0·715, almost the
same as the line drawn through the points of Regnault's obser-
vations below the boiling-point. Both in its node and its upper
limit this liquid is exceptional.

§ 26. This is no proof of my temperatures being at all to be
compared in point of standard accuracy with those of Regnault,
which indeed it would be absurd to imagine, as the thermome-
ters employed were common German chemical thermometers
with glass scales, and the correction to reduce to the air-thermo-
meter was taken from a Table afterwards published in the Phil.
Mag. vol. xxi. (June 1861). Coincidence of node may accom-
pany considerable divergence of temperature if that divergence
is gradual. The following is an example.

§ 27. M. Avogadro's observations of the tension of the vapour
of mercury under the boiling-point * are to be found projected
on the original chart of 1852. I have again projected the points
on chart R, Plate III. (which has the same scales as Plate I.),
with original temperatures by thermometer of mercury, and the
same corrected to air-thermometer. A line was drawn through
the latter as shown ; and this line was afterwards transferred to
the small-scale general chart, Plate III. The exact direction of
this line to the ether-node is curious, as the boiling-point is
nearly 20° below that of Regnault's mercury projected along-
side. The temperatures are by air-thermometer.

§ 28. A few other liquids were tried, each in two tubes. One
of these, the chloride of sulphur (a small specimen of which was
prepared for me by a professional chemist), shows a very exact
conformity with the law from 160° to 210° ; and a curious ano-
maly presents itself when this line is produced downwards. It

* *Ann. de Chim. et de Phys.* vol. xlix. p. 369.

cuts the axis at $-274°$. The dichloride was also tried, in two tubes but the points did not range well; the general trend was parallel to the chloride. It may be that the true line converges to $-274°$, certainly not to the ether-node.

Vapour-density and Liquid volume at Point of Transition.

§ 29. The following are the extracts from an unpublished paper giving an account of these observations, made in 1852.

" The chief object of the following experiments was to ascertain if the law of density of saturated vapours holds good up to that point where, according to M. Cagniard de la Tours's interesting researches, the liquid condition seems to terminate suddenly. The observations were made on the same principle as those which were the means of detecting the general law of density, the details of which have been communicated to the Royal Society. The tubes were mostly from 2 to 3 inches in length. The graphical method was employed to compute vapour-density and liquid-volume (see Phil. Mag. vol. xxvi. Appendix II. to paper on Expansion of Water).

" The following was the method employed to heat the tubes and take the temperatures. A glass funnel, about 3 feet long and 1 inch in diameter, was fixed vertically over a large Argand oil-lamp. One of the prepared tubes was placed in a small brass wire frame arranged and fitted so as to slip into the top of the funnel and hold the tube fixed steadily at the centre of the current of heated air about 4 or 5 inches below the top. By increasing the flame of the lamp gradually, the transition temperature was attained, and by careful adjustment was kept nearly steady. The liquid volume being noted, the tube was taken out and a thermometer put exactly in its place. The mercury, quickly rising, became steady, the temperature was noted, and thermometer removed. A second tube, having a different proportion of its volume filled with the same liquid, was slipped into the same place; then a third, and a fourth.

" The state of the liquid in the tube was closely examined through a watchmaker's lens by transmitted light. The tubes were generally of hard glass $\frac{1}{8}$ inch bore and $\frac{1}{50}$ inch thick. When carefully sealed they did not burst at the transition-point of any of the liquids, except water, which burst the tube at about $330°$, first corroding the glass in a ring at the top of the liquid.

" The liquids observed by this method were ether, alcohol, sulphide of carbon, water, chloroform, glacial acetic acid, dichloride of sulphur, turpentine, and sulphuric acid.

"*Ether.*—Boiling-point $41°$; four tubes; transition-point $221°$; density of vapour $0·19$ to $0·23$; density of liquid $0·43$ by third and fourth tubes (unity at $29^{c}·5$). By two of the tubes the den-

sity of vapour was found to be 0·23, which is exactly the value computed from the line of density.

"*Alcohol.*—Boiling-point 79·5 ; four tubes ; transition-point 281°. Five series of observations in good accordance. Density of liquid 0·48, and of vapour 0·222. The same computed from gradient is 0·245.

"*Sulphide of Carbon.*—Boiling-point 49° ; five tubes ; point of transition 302°. The second, fourth, and fifth tubes give density of vapour 0·305, and of liquid 0·45. The vapour-density computed from the gradient is 0·305.

"*Chloroform.*—Boiling-point 60° ; three tubes ; transition-point 266° ; density of liquid 0·42, of vapour 0·24.

"*Glacial Acetic Acid.*—Three tubes ; no distinct point of transition. The liquid surface gradually fades away at about 315°, but density of lower part greater than upper ; no activity manifested in the tube ; density of liquid about 0·40 to 0·44, and of vapour from 0·14 to 0·18.

"*Dichloride of Sulphur.*—Four tubes ; transition temperature estimated at about 500°, at which the liquid and the vapour are of the *same* density, nearly 0·35 (the liquid unit density at 29°·5).

" Turpentine shows singular phenomena of change of colour (becoming scarlet before transition) and decomposition. On cooling, after transition, the liquid was thick and oily, deep green by reflected light, and reddish brown by transmitted. On opening the point of the tube there was a violent rush of gas and effervescence of the liquid, which had first the odour of pitch, then of creosote, and then naphtha, but had lost that of turpentine.

" It was remarked in these observations that near the transition-point the rate of apparent liquid-expansion becomes so very great that it is difficult to keep the liquid surface steady ; it rises and falls like a sensitive air-thermometer. The capillary attraction ceases, and from being concave the surface becomes first quite flat, then convex like mercury."

§ 30. The law of saturated vapour-density thus appears to be strictly maintained from the zero of vapour up to the transition-point. It is not altered by the liquid becoming solid (Regnault), and is uninfluenced by the abnormal expansion of water. The liquid molecules of water are abnormal in their change of volume, while the vapour-molecules in contact with them behave as if they were subject to the influences common to all the other liquids expanding in the normal manner.

Evidence as to the Law of Liquid expansion.

§ 31. This is given in Plate IV., where the values of $\dfrac{dt}{dv}$ are

projected to *t* in thirteen cases, which include the most accordant, Nos. 1 to 8, and the least accordant, Nos. 12 to 13. The most remarkable is sulphurous ether, No. 6. The first series of five observations are in perfect accordance with the theory, and prove the extreme accuracy of M. Pierre in this and several others, which are almost as good. In other cases, as Nos. 11, 12, 13, where the law of continuity is not maintained, it appears as if some chemical disturbance had taken place in the liquid during the process of heating.

M. Pierre has submitted forty-four chemically pure liquids to thermometric trial from $0°$ up to their boiling-point, and several of them from $0°$ down to $-30°$. I have graphically examined and analyzed all but a very few. Some of them with high boiling-points present a clear range of about $100°$; and the straightness of the line of $\frac{dt}{dv}$, in which the presumed law of expansion consists, is well developed (see Nos. 3, 4, 5, 6, 7, 8, 9).

Those with boiling-point under $100°$, when regular, afford the means of computing the constants γ and P_0 of the equation $\frac{dt}{dv} = P_0(\gamma - t)$,—although the range is too small to prove the law, except through the value they give to γ being in accordance with the principle shown by Plate III., that causes the upper limiting temperature, γ, of many of the liquids whose lines of vapours trend to the ether-node to range in a line parallel to the axis of temperature.

§ 32. In most of these M. Pierre has given for each observation the value of *a*, the mean expansion from $0°$. Thus, 1 being the volume at $0°$ and *v* the same at $t°$, $a = \frac{v-1}{t}$. The projection of these values of *a* as ordinates to *t* ought to present a series of points in a curve convex to the axis of temperature: chart Q, Plate IV., is an example of this projection in the case of the three ethers—hydrochloric, hydrobromic, hydriodic. The first has too small a range; but it will be remarked that the upper four points keep well in a line, and that three are exact. This makes it probable that they are sufficiently accurate. Accordingly, the two observations at the points marked A, B are selected to compute γ and P_0, as follows :—Let $t_0\,t_1$, $v_0\,v_1$ be the respective temperatures and volumes at those points having reference to the unit volume at $0°$. We have

$$\frac{t_0}{v_0-1} = \frac{dt}{dv} = P_0(\gamma - \tfrac{1}{2}t_0)$$

= the reciprocal of the absolute increment of volume at $\tfrac{1}{2}t_0$, and

$$\frac{t_1 - t_0}{v_1 - v_0} = P_0[\gamma - \tfrac{1}{2}(t_1 + t_0)]$$

= the same at $\dfrac{t_1 + t_0}{2}$; hence we obtain $\gamma = 186°·4$, and $P_0 = 3·485$

($t_0 = 14°·51$, $t_1 = 26°·41$, $v_0 = 1·02326$, $v_1 = 1·04386$).

The previous values by M. Drion's observations were $\gamma = 187°$ and $P_0 = 3·545$.

The next line (D C) on chart Q was drawn through the *a* points of M. Pierre's hydrobromic ether by means of a thin flexible steel straight edge. To judge the value of such a set of points, a light pencil-line is drawn in the general trend, and then the middle points are examined to see if there are any parallel to this line; if so, the straight edge (set on its edge) is brought to them and bent up a little on each side so as to pass over or through the extreme points if possible. The result, it will be observed, is favourable; the points C and D are selected for computation, from which is obtained $\gamma = 253°$ and $P_0 = 2·97$; the greatest discrepancy is at $28°$, where the divergence is $0°·18$.

In this way the points for hydriodic ether were also treated, and E, F selected, from which $\gamma = 312°$ and $P_0 = 2·75$. The greatest divergence is at $58°$, where it amounts to about $0°·2$.

A similar projection was made with the short series of observations on sulphuric ether* : the points ranged well; the two selected were $23°·36, ·03657$; $38°·14, ·06216$, which give $\gamma = 211°$, $P_0 = 3·21$. Others give γ various up to $250°$.

§ 33. The series on chloroform† was graphically examined, and the three highest were found very exactly in a line, giving $\gamma = 334°$, $P_0 = 2·52$; but the lower observations gave points which were quite out of range, and showed that the law of continuity was not maintained; the divergence amounts to nearly $1°$.

The series on chloride of silicon and chloride of phosphorus are also wanting in regularity.

§ 34. The series on the *bichloride of carbon* are good; they give $\gamma = 318°$, $P_0 = 2·73$. The *bromide of hydrocarbon* is No. 5 of Plate IV. On extending the general line it cuts the axis at $\gamma = 440°$. If the two lower points are preferred, the line passes through the upper point and cuts the axis at $423°$.

Turpentine is No. 7 of Plate IV.; the line cuts the axis at $461°$.

The vapour-lines of all these liquids have been fixed by Regnault's observations, which are projected on Plate I., and they all trend to one point at the absolute zero of temperature, called the ether nodal point, shown in Plate III.

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* *Ann. de Chim. et de Phys.* vol. xv. p. 361.

† Ibid. vol. xxiii. p. 208.

§ 35. The next step is to lay off these values of γ on the respective lines. This has been done on Plate III. and the points marked γ. Considering that the distance of these points from 0° depends on the value obtained for P_0, which depends on the integrity of the second differences of expansion, its mathematical expression being $\frac{d^2v}{(dv)^2}$, we have to judge whether, if perfect exactness had been attained in it and direction of line of vapour-density, they would have ranged in one line parallel to the axis of temperature, except sulphide of carbon. In favour of this there is to be added that if we compute γ from Pierre's observations on a liquid (*e. g.* bromine, methyle-bromide, &c.) whose vapour-line has not yet been determined, but which we may judge from analogy is likely to trend to the ether-node, and which we assume to do so by drawing a line from this node through the boiling-point of the liquid and extending it upward to γ, we find invariably that this point ranges along with the others. They are marked $\overset{|}{\underset{|}{\bigcirc}}$γ on Plate III.

§ 36. The dotted line *l* G is drawn parallel to the axis at a distance, *z l*, equal to three times the distance of the ether-node, *z n*. It will be remarked that it coincides with the average range of the upper limiting points γ, γ, &c.

This closes the evidence of the law of saturated vapour-density and of liquid expansion,—also of the ether nodal point, and of the line of the upper limiting temperatures γ. We now come to the

Evidence as to Relations of Molecular Volume in different Liquids.

§ 37. If we draw a line parallel to the axis of temperature intersecting the vapour-lines in the respective points τ, τ, &c. (Plate III.), it is evident that the molecular density of the respective saturated vapours at those points is the same in all (§ 4); *i. e.* the number of molecules in a cubic inch of each is the same in all; in other words, the volume of the *aëriform* molecule is the same in all. If we now compute the volume of the *liquid molecule* at these points or τ temperatures, we shall find that they also are quantitatively related to each other in a very interesting way.

§ 38. The vapour molecular volume of a body is the vapour-density (*i. e.* hydrogen 1, oxygen 16, water 9, alcohol 23, &c.) divided by the specific gravity of the saturated vapour at the respective temperatures. The liquid molecular volume is the same vapour-density of the body divided by the specific gravity of the liquid at the respective temperatures. It has now to be shown that in certain chemically allied bodies these latter volumes,

measured at τ temperatures, are proportional to the h tangents (§ 4) respectively.

§ 39. To find this tangent, we take two points in the line of vapour (Plate I.), and measure by scale, first the difference η of the ordinates at those points, and second the difference θ of the temperatures. The quotient $\dfrac{\theta}{\eta} = h$. Thus the easy plan is to select the points so that $\eta = 1$, which gives $\theta = h$, the constant of that particular line of vapour.

§ 40. As a convenient point through which to draw the line parallel to the axis upon which τ temperatures have to be measured, we may take the intersection of the muriatic-ether-line with $0°$ C. This is drawn on Plate III. It intersects the hydrobromic-ether-line at $27°\!\cdot\!4$. The vapour-density of this ether is $54\cdot5$ (on hydrogen scale), and spec. grav. at $0°$ $1\cdot473$; the volume at $27°\!\cdot\!4$ by Pierre's observations is $1\cdot0387$ (volume at $0°$ unity). Hence, to find the liquid molecular volume at $27°\!\cdot\!4$, the τ temperature, we have to compute $\dfrac{54\cdot5 \times 1\cdot0387}{1\cdot473}$, which comes out $38\cdot43 = \mu$ of hydrobromic ether.

The hydriodic-ether-line intersects the τ line at $62°\!\cdot\!4$, at which temperature the volume is $1\cdot082$; the vapour-density is 78, and spec. grav. at $0°$ $1\cdot975$; we have $\dfrac{78 \times 1\cdot082}{1\cdot975} = 42\cdot73 = \mu$ of hydriodic ether.

Now h of the first is $158\cdot6$, and of the second 177 (as may be computed from the chart, Plate I.). *These are in the same ratio as the respective values of* μ. Thus $\dfrac{158\cdot6}{38\cdot43} = 4\cdot12$, and $\dfrac{177}{42\cdot73} = 4\cdot14$, that is, $\dfrac{h}{\mu}$ = a constant.

The τ temperature of the muriatic ether is $0°$, spec. grav. $0\cdot920$, vapour-density 32, and $h = 144$; hence to find μ we have $\dfrac{32}{0\cdot92} = 34\cdot78$, and $\dfrac{h}{\mu} = \dfrac{144}{34\cdot78} = 4\cdot14$, the same as the preceding.

Chloroform intersects the τ line at $51°\!\cdot\!4$, where the volume by Pierre is $1\cdot0664$, vapour-density 60, spec. grav. at $0°$ $1\cdot525$, $h = 171$: to find μ, there is

$$\frac{60 \times 1\cdot0664}{1\cdot525} = 41\cdot96, \text{ and } \frac{h}{\mu} = \frac{171}{41\cdot96} = 4\cdot08.$$

The mean of these four values of $\dfrac{h}{\mu}$ is $4\cdot11$.

§ 41. By inspecting fig. 1 it will be seen that measuring the temperatures on the τ line implies that the absolute temperatures,

i. e. the temperatures reckoned from $-274°$, the zero of gaseous tension, are taken in the same ratio as the respective values of h, the tangents or exponents of the thermomolecular lines.

§ 42. The next point to consider is, that if the above ratio of molecular volume holds good throughout the whole range of expansion, the *proportionate* dilatation at the τ temperatures ought to follow the same ratio of h inversely, or, expressed by symbols, $\dfrac{vdt}{dv} \propto h$ (in which $dt = 1°$), because, if we imagine the τ line to move upwards parallel to itself through a small increment of its distance from the axis of temperature, it cuts off at each intersection with a vapour-line an increment of temperature proportional to h, and, to maintain the same ratio in the molecular volumes at the end as at the beginning of these increments, the *proportionate dilatations* should be all equal to each other—which can only take place if the proportionate increment corresponding to a constant value of dt or $1°$ is inversely as h. This increment, therefore, multiplied by h, should be a constant quantity in all these four liquids. This product being a fractional quantity, we compute its reciprocal $\dfrac{vdt}{dv} \cdot \dfrac{1}{h}$ from the constants of the three ethers found in § 32.

Muriatic Ether.—The τ temperature is $0°$, at which $v = 1$, hence
$$\frac{vdt}{dv} = \frac{dt}{dv} = P(\gamma - t) = P\gamma = 3\cdot48 \times 186\cdot4 = 649;$$
and h being 144, we have $\frac{649}{144} = 4\cdot50$.

Hydrobromic Ether.—The τ temperature is $27°$, at which $v = 1\cdot0385$*, $P = 2\cdot97$, $\gamma = 253$, and $P\gamma - t = \dfrac{dt}{dv} = 671$, which, $\times$ by v and $\div$ by $h = 158\cdot6$, gives $4\cdot39$.

Hydriodic Ether.—The τ temperature is $62°\cdot4$, at which $v = 1\cdot0782$, $P = 2\cdot75$, $\gamma = 312°$, $P(\gamma - t)v = 742$, which, divided by $h = 176\cdot9$, gives $4\cdot19$. A previous result by another computation is $4\cdot32$.

Chloroform.—The τ temperature is $51°\cdot4$, at which $v = 1\cdot0660$†, $P = 2\cdot52$, $\gamma = 334$, $h = 171$. These give the quotient $4\cdot48$. The mean of the four is $4\cdot38 = \dfrac{vdt}{dv} \cdot \dfrac{1}{h}$ for these four liquids.

§ 43. The product of this by the previous constant $\dfrac{h}{\mu}$ gives $\dfrac{vdt}{dv} \cdot \dfrac{1}{\mu} = 18\cdot00$, which is also a constant at the respective τ temperatures of these four liquids. This third constant is indepen-

* *Ann. de Chim. et de Phys.* vol. xv. p. 369.
† Ibid. vol. xxxiii. p. 208.

dent of h; it expresses merely the ratio of molecular volume to proportionate expansion at τ, and is found to have the same value in the bromide of hydrocarbon and some others where the first two constants do not conform. *E. g.* :—

Bromide of Hydrocarbon.—The τ temperature is $127°$, at which $v = 1·1180*$, vapour-density 94, $P = 2·61$, $\gamma = 423$, $h = 211·2$, $\mu = \dfrac{1·118 \times 94}{2·207} = 47·62$, $\dfrac{h}{\mu} = 4·43$ (instead of $4·11$), $\dfrac{vdt}{dv} \cdot \dfrac{1}{h} = 4·09$ (instead of $4·32$). The product of these is $18·11$, almost the same as the preceding mean.

The same is the case with chloride of hydrocarbon and protochloride of arsenic. They would conform to the first group entirely, if the values of their h tangents were reduced about $\frac{1}{14}$ part.

§ 44. A large proportion of the liquids examined by M. Pierre have not their vapour-lines established; but if we assume them to issue from the ether-node, and join that point and their boiling-point on the general chart (Plate III.), we may then lay off the upper limit γ upon this line produced; and if it range near to the dotted line, it is probably correct. This is the case with the hydrobromate, hydriodate, and probably the hydrochlorate of methyle, which have the quotients $\dfrac{h}{\mu}$ &c. alike.

The bichloride of tin and bichloride of silicium are also thus united. Other symmetric relations are indicated in the Table before me, which includes most of Pierre's liquids; but it would be hazardous to proceed further in this direction without the complete data.

Evidence of Relations with respect to the Cohesion-Integral of a Molecule in different Liquids.

§ 45. Let $Q =$ quantity of heat given out by a pound of a certain liquid in descending from $t°$ to $0°$, and $X =$ quantity of heat given out by a pound of the same body in the condition of saturated vapour at t in passing into a liquid state and descending to $0°$. Then $X - Q = C$, the quantity of heat required to change the condition of a pound of the same body from liquid to saturated vapour without performing work—in other words, the integral of liquid cohesion at t.

Regnault has determined X and Q for a number of bodies through a considerable range that includes the t temperatures of some of our liquids whose thermomolecular lines are well established. We have thus the data for computing C at such temperatures, which are near the respective boiling-points. By

* *Ann. de Chim. et de Phys.* vol. xx. p. 41.

multiplying this value of C by ω, the vapour-density or *molecular* weight (not atomic weight) of the body, we obtain a number that represents the cohesive integral of *a molecule* of that body at the τ temperature.

Performing this computation for several bodies and comparing the numbers with the respective values of h and of μ, if it is found that they follow the same ratio, that $\dfrac{C\omega}{\mu}$ is a constant quantity at the τ temperatures of the several liquids, the legitimate inference to be drawn is that the cohesive force of each molecule is proportional to its volume μ when in the liquid state. This is equal to $\dfrac{\omega}{s}$, the quotient of vapour-density by spec. grav. at τ, and hence $\dfrac{C\omega}{\mu} = Cs$ is constant in the group of liquids. The following is the computation.

Muriatic Ether.—At pp. 912, 914 of Regnault's second volume we have two values of X : one at $+12°{\cdot}2$ is $97{\cdot}70$; another at $-7°{\cdot}2$ is $95{\cdot}88$. The τ temperature of this body being $0°$, we have X at $0° = 96{\cdot}60 = C$ in this case, as $Q = 0$. The vapour-density is $32\frac{1}{4} = \omega$ and $C\omega = 3115$, which, divided by $h = 144$, gives $21{\cdot}63$ as the value of the quotient $\dfrac{C\omega}{h}$.

Hydriodic Ether.—$X = 53{\cdot}20$ at $-5°$, and $58{\cdot}9$ at $71°$. The τ temperature is $62°{\cdot}4$, at which (p. 278) $Q = 10{\cdot}4$, and $X = 58{\cdot}3$; hence $C = 47{\cdot}9$, $\omega = 78$, $h = 177$, $\dfrac{C\omega}{h} = 21{\cdot}11$.

Chloroform.—At p. 836, $X = 74{\cdot}00$ at $51°{\cdot}4$, the τ temperature, and $Q = 12{\cdot}07$ (p. 276); hence $C = 61{\cdot}9$. And since $\omega = 60$, $h = 171$, we have $\dfrac{C\omega}{h} = 21{\cdot}71$.

Sulphuric Ether has $\dfrac{h}{\mu} = 3{\cdot}00$ instead of $4{\cdot}11$, the value common to the three preceding liquids ; nevertheless the cohesion-integral of its liquid molecule has the same ratio to h. Its τ temperature is $24°$, at which $Q = 12{\cdot}86$ (p. 275) and $X = 105{\cdot}2$ (p. 820); hence $C = 92{\cdot}3$ and $\omega = 37$, $h = 156{\cdot}7$ gives $\dfrac{C\omega}{h} = 21{\cdot}79$. The mean of the four values is $21{\cdot}56$.

In the same way the quotient was computed for the bichloride of carbon $20{\cdot}2$, sulphide of carbon $21{\cdot}1$, turpentine $19{\cdot}1$, chloride of phosphorus $20{\cdot}0$.

§ 46. It seems probable that this value of $\dfrac{C\omega}{h}$ is the same for

all liquids which belong to the ether-node. I find that by taking C from Professor Andrews's observations on latent heat at the boiling-point, which corresponds nearly to the τ temperature, and computing therewith $\dfrac{C\omega}{h}$, a value of about 21 always appears in those cases that are likely to belong to the ether-node class.

§ 47. A higher value seems to belong to liquids that belong to the water-node; thus $\dfrac{C\omega}{h}$ for water is 30·4, and for pyroxylic spirit 29·25. For alcohol a still higher value is found, viz. 35·7; and its line cuts the zero-line $z\,q$ (fig. 1) still further down than the water-node.

§ 48. The latent heat of chloroform, of sulphuric ether, and of some other bodies have been determined by Regnault up to high temperatures, so that we are enabled to test the presumed law at a higher value of τ. I have computed the values of C corresponding to all the values of X (making use of the empirical formula for Q), and laid them off as ordinates to the respective temperatures ; then, having drawn the curve by flexible straight edge, the value of C at the respective τ temperatures is read off and $\dfrac{C\omega}{h}$ computed.

Let $120° =$ the new τ temperature of sulphuric ether; a parallel to the axis drawn through this point (Plate III.) cuts the chloroform line in 157°. At these temperatures the respective values of C are 73·2 and 49·4, which give 17·23 and 17·31 as the respective values of $\dfrac{C\omega}{h}$, an accordance that is surely very remarkable.

§ 49. Let us now compare C at different temperatures of the *same* liquid with the volume v at those temperatures. First, sulphuric ether, the expansion constants of which are determined from Pierre to be in conformity with the general law ($\gamma = 224$, $P_0 = 3\cdot01$). I take from the curve of C 91·7 at 20°, and 78·0 at 100°,—the volumes at these temperatures being respectively 1·031 and 1·199. Hence we have 13·7, the difference of C, equivalent to 0·168, the corresponding difference of v. In the same proportion, $13\cdot7 : 0\cdot168 = 78\cdot0 : 0\cdot957$, the augmentation from 100° up to the maximum volume at transition, if $\dfrac{-\delta C}{\delta v}$ is constant. This gives 2·156 as that maximum when C is reduced to zero. Now the temperature corresponding to this volume, computed from the above value of γ and P, is 217°. The observed temperature of transition was 221° (§ 29), and maximum

volume 2·44. I may add that the volume computed for −274° is 0·828, nearly one-third of the maximum.

Chloroform treated in the same way (but leaving out the highest observation of X, which is quite out of the line of the others) gives 268° as the temperature when C=0. The computed volume at that point is 2·02. The transition temperature observed was 266° (§ 29), and maximum volume 2·43. The volume computed for −274° is 0·847.

Sulphide of carbon treated in the same way gives transition-volume 2·15, the observed being 2·22, and at −274° the computed is 0·852.

These computations all tend to show the probably simple relation between liquid molecular volume and cohesion-integral, —the absolute value of the increment of the one having always the same ratio to the absolute value of the decrement of the other in the same liquid and in the same class of liquids (where $\dfrac{h}{\mu}$ has the same value).

§ 50. In liquids, such as chloroform and sulphuric ether, which are not related in molecular volume but have $\dfrac{C\omega}{h}$ common to both, the following computation suggests the question as to whether the force required to effect the *same absolute increase of volume* (or, in other words, the heat-force rendered latent) is proportional to the molecular weight or vapour-density. One ounce of *ether* absorbs 16·25 unities of heat in expanding from 0° to 100°; 1 cubic foot of it weighs 736 oz., and thus absorbs 11960 unities in expanding from 0° to 100°, during which its volume is augmented from 1 to 1·2 cubic foot.

One ounce of *chloroform* absorbs 13·25 unities of heat in expanding, so as to augment its volume from 1 to 1·2. 1 cubic foot of chloroform weighs 1525 oz., and thus requires

$$1525 \times 13\cdot25 = 20206 \text{ unities}$$

to increase its liquid volume from 1 to 1·2 cubic foot. Now mark the ratio 11960 : 20206 = 37 : 62·5, which is nearly the ratio of the respective values of ω, viz. 37 : 60; that is, nearly, considering the difficulty of obtaining $\dfrac{\delta C}{\delta v}$ exactly.

A cubic foot of the sulphide of carbon at 0° requires 15·5 × 1293 = 20041 unities to become 1·2 cubic foot. This is nearly the same amount as chloroform and the three halogen ethers, although the relation of molecular volume is not so simple.

§ 51. The following Table contains the thermomolecular con-

stants of a few liquids belonging to the ether-node, brought together as an example of the mode of arrangement adopted after some experience.

Note.—The number in line 12 under turpentine is rather small, to be in accordance with the law of uniformity. The paucity of observations on this liquid perhaps may account for the want of precision. The constants of expansion for the hydrochloric ether were taken from M. Drion's observations, and the others from Pierre; hence perhaps the inequality at 16, 19, 20.

No.		Hydrochloric ether, $H^2C.H^{\frac{1}{2}}Cl^{\frac{1}{2}}$.	Hydrobromic ether, $H^2C.H^{\frac{1}{2}}Br^{\frac{1}{2}}$.	Hydriodic ether, $H^2C.H^{\frac{1}{2}}I^{\frac{1}{2}}$.	Chloroform, $ClC^{\frac{4}{2}}.H^{\frac{1}{2}}Cl^{\frac{1}{2}}$.	Ether, $H^4C^2.HO^{\frac{1}{2}}$	Turpentine, H^8C^5.
1	ω weight of molecule.	$32\frac{1}{4}$	$54\frac{1}{2}$	78	60	37	68
2	Boiling-point	$12°·2$	$38°·5$	$71°$	$60°·8$	$35°$	$157°$
3	Spec. grav. at 0°	$0·920$	$1·473$	$1·975$	$1·525$	$0·736$	$0·872$
4	h	144	$158·6$	177	$171·1$	$156·7$	226
5	τ	0	$27°·4$	$62°·4$	$51°·4$	$24°$	$155·4$
6	v at τ	$1·000$	$1·038$	$1·082$	$1·066$	$1·038$	$1·176$
7	μ at τ	$34·74$	$38·31$	$42·67$	$41·96$	$52·15$	$91·7$
8	$\dfrac{h}{\mu}$ at τ	$4·14$	$4·14$	$4·10$	$4·08$	$3·00$	$2·46$
9	C at τ	$96·6$	......	$47·9$	$61·9$	$92·3$	$63·3$
10	$C\omega$ at τ	3115	......	3736	3716	3415	4305
11	$\dfrac{C\omega}{\mu}$ at τ	$89·5$	......	$86·5$	$88·6$	$65·5$	$47·0$
12	$\dfrac{C\omega}{h}$ at τ	$21·63$	......	$21·11$	$21·71$	$21·79$	$19·1$
	„ at τ_1	......	......	......	$17·23$	$17·31$	
	hyp. $\log \left(\dfrac{\gamma}{\gamma - t} \right) = P_0(v-1)$.						
13	γ	$185°$	$254°$	$312°$	$(282°)$	$224°$	$461°$
14	P_0	$3·65$	$2·95$	$2·89$	$(2·97)$	$3·01$	$2·34$
15	G	$459°$	$528°$	$586°$	$(556°)$	$498°$	$735°$
16	$\dfrac{G}{h}$	$3·19$	$3·32$	$3·31$	$(3·26)$	$3·18$	$3·26$
17	$\dfrac{vdt}{dv}$ at 0°	673	749	887	839	614	1080
18	$\dfrac{vdt}{dv}$ at τ	673	694	764	759	562	843
19	$\dfrac{vdt}{dv} \cdot \dfrac{1}{h}$ at τ	$4·67$	$4·38$	$4·32$	$4·43$	$3·59$	$3·74$
20	$\dfrac{vdt}{dv} \cdot \dfrac{1}{\mu}$ at τ	$19·36$	$18·11$	$18·00$	$18·09$	$10·77$	$9·19$
21	$\dfrac{\delta C\omega}{\delta \mu}$	91	......	95	97	61	42

§ 52. The relation between liquid molecular volume and liquid molecular cohesion (line No 11) strikes the attention as being undoubtedly *causal*. Also the relation exhibited in line 12

shows cohesion of a molecule as the potential antecedent of the inclination of its thermomolecular line.

§ 53. M. Pierre has subjected four liquids to examination which are closely related to each other by chemical substitution. These are the Dutch liquid $H^2 C Cl$ and $H^{1\frac{1}{2}} Cl^{1\frac{1}{2}} C$, $HC Cl^2$, $H^{\frac{1}{2}} C Cl^{2\frac{1}{2}}$. The boiling-points are 85°, 114°·2, 138°·5, and 153°·5 ; and if their lines issue from the ether-node, the respective values of h are 187, 198, 212, 220 ; and $\dfrac{G}{h}$ is constant for all, being the same as in line No. 16 of the above Table ; so it is satisfactory evidence of their belonging to the ether-node. But $\dfrac{h}{\mu}$ varies from 4·4 to 3·1 ; so there is no relation between molecular volume and slope of their lines. They are, however, connected by the proportion which holds good between their tangents h and their proportionate dilatations at the respective τ temperatures. This ratio, $\dfrac{vdt}{dv} \cdot \dfrac{1}{h}$ (of line No. 19, Table), is the same in all, and equal to 4·00 very nearly. If $\dfrac{C\omega}{h}$ is constant, as in line 12 of Table, then $\dfrac{vdt}{dv} \cdot \dfrac{1}{C\omega}$ is also constant ; so that in these substitutional liquids the proportionate expansion for increments of temperature respectively proportional to h or $C\omega$ is the same in all. Thus, while the integral cohesion of a molecule determines h as usual, the *proportionate* expansion for intervals of τ temperature is the same in all, although there is no apparent relation between their *absolute* molecular volumes.

§ 54. In employing chemical symbols in this inquiry, it is necessary to express the *molecule* of a compound in terms of the *molecules* of its constituents, not of the *atoms*. This is done by simply dividing the usual atomic formulæ by 2, unless when arsenic, phosphorus, selenium, or sulphur is involved—the divisors being then 4 for the first three, and 6 for the last.

It would be a boon to molecular physics if chemists could do without the word *atom*, and substitute in its place *molecule, half-molecule, quarter-molecule*, &c. Thus an atom of mercury is a molecule ; an atom of cadmium is a molecule ; an atom of oxygen is half a molecule ; an atom of phosphorus is one-fourth of a molecule, &c. An atom of ether is a molecule, which denote by the letter E. An atom of sulphurous acid is a molecule, which denote by the letter U. An atom of sulphurous ether is a molecule, which denote by the letter Q.

$Q = UE = O^2 S . C^4 H^8 . H^2 O$, in which the letters signify *atoms*, some of which are *half* molecules, some *whole* molecules, and one represents the *sixth* part of a molecule.

$Q = U . E = OS^{\frac{1}{6}} . C^2 H^4 . HO^{\frac{1}{2}}$, in which the same letters, *all without any exception,* signify *molecules*, each of which, when it stands by itself, occupies a volume. U E indicates two volumes changed into one. $C^2 H^4 HO^{\frac{1}{2}}$ indicates $2 + 4 + 1\frac{1}{2} = 7\frac{1}{2}$ volumes changed into one, and $OS^{\frac{1}{6}} . C^2 H^4 HO^{\frac{1}{2}}$ indicates $8\frac{4}{6}$ volumes changed into one.

Applications of this system to express chemical reactions are given in the Philosophical Magazine for April 1864. It renders unnecessary the tedious ever recurring verbal description of constitution by volume given by chemical writers; and while thus saving space, would, I am fully convinced, put an end to the confusion which is still admitted to exist by M. Wurtz (see last sentence of the first part of the recently published 'Introduction to Chemical Philosophy'), in spite of the new system of notation which he proposes.

XII. *Investigation of the Electric Light.*
By Professor E. Edlund[*].

1. EVERY natural force has a definite quantitative action. If under one set of circumstances a force exerts an action which in any respect differs from that which the same force produces under other circumstances, both actions must still be quantitatively equal. If the force produce both actions simultaneously, the sum of the actions must be as great as the quantitative value of one of them when this alone is produced. It is of course presupposed that the time during which the force acts is equal in all these cases. The voltaic current exerts, as is well known, various actions; it produces heat and light, decomposes compounds which are conductors of electricity, excites magnetism, and acts upon bodies already magnetic, induces voltaic currents in adjacent conductors, &c. In a certain sense it may be said that the first and direct action of the voltaic current is the production of heat, because this always accompanies it, while the other actions require certain conditions for their fulfilment. It is known from trustworthy experiments that the heat produced is proportional to the square of the intensity of the current multiplied by the resistance. The entire quantity of heat which is developed by the current is therefore propor-

tional to the square of the electromotive force divided by the entire resistance of the circuit. This holds good so long as the current performs no other work than the production of heat. That this law deduced from experiment is correct may be regarded as proved, since, as Clausius has shown*, it may be theoretically deduced. But if the current at the same time that it produces heat performs other work, the quantity of heat developed must be diminished by an amount corresponding to this work. Hence, if we have a voltaic battery of given electromotive force, whose poles are joined by means of a solid conductor, and if besides the electromotive force we know both the internal and external resistance of the battery, the quantity of heat developed during a certain time may easily be calculated. Assume, now, that part of the external resistance is removed, and in its place is inserted a decomposable liquid (dilute sulphuric acid for instance) the resistance of which is equal to that part of the solid conductor which has been removed, by this exchange the electromotive force and the resistance will have undergone no alteration. Yet the heat produced cannot be so great as before, since the current, along with the production of heat, performs the mechanical work necessary for chemically decomposing the water. This is due to the circumstance that, when water is decomposed into hydrogen and oxygen, there is an absorption of heat, and that this absorption is equal to the heat produced when hydrogen combines with oxygen. Hence the absorption furnishes a measure of the work necessary for the decomposition. The entire quantity of heat produced by the current will be diminished by an amount which corresponds to the work of decomposition effected by the current. The coating of the electrodes with hydrogen and oxygen, by which is produced a current in the opposite direction to the principal one, is an entirely secondary phenomenon which has nothing to do with the essence of the case.

Further, if we have a voltaic current whose total resistance is known, and whose intensity is continually changing, the total heat produced by the current can be calculated if the intensity at each moment is known. If a closed circuit be placed in the neighbourhood of the principal current, an induced current is developed in it. The primary current produces voltaic induction simultaneously with the production of heat; and it is clear that the production of heat must be less than when there is no induction. But, on the other hand, the electromotive force of the battery and the resistance of the principal conductor, on which, in accordance with the law mentioned above, the production of

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* Poggendorff's *Annalen*, vol. lxxxvii. p. 415.

heat depends, have not been altered. In a former investigation*
I have experimentally proved that in the present case the heat
produced in the primary circuit is in fact less; and in all cases
the sum of the heat produced by the principal current, and of
that developed in the path of the induction-current, is equal to
the heat which would be produced by the principal current
alone if there were no induction. But as the heat which the
induction-current developes is justly regarded as the thermal
equivalent of this current, it follows that the heat produced in
the primary current during induction has been diminished by
the quantity of heat which corresponds to the work which the
principal current consumes in producing induction. As I have
shown in the above-mentioned research, this diminution in the
production of heat in the principal current is produced by the
circumstance that the induction-current developes induction-
currents of higher order in the principal conduction, which add
to or subtract from the principal current in such a manner that
the heat produced is always diminished. Thus in this case the
quantity of heat produced would be diminished by means of the
induction-current. We assume, finally, that the conducting-wire
between the poles of the battery is connected with a coil of
covered wire, and that in this coil there is a soft-iron cylinder
whose keeper is removed from the iron cylinder as soon as the
magnetism developed is too feeble to attract it to the poles of
the electromagnet. Now if the current be opened and closed at
definite intervals during a certain time, a definite quantity of
work is produced. If, then, the keeper while it is being attracted
towards the magnet be caused to perform mechanical work (by
raising a weight for instance), it is clear that the heat produced
will be diminished by an amount corresponding to the work
performed, which, indeed, Favre has experimentally proved† is
actually the case. On the other hand, neither the resistance in
the battery nor the electromotive force, the points on which the
heat developed depends, has been changed. Yet it may easily
be seen that the different behaviour of the induction-currents
in the two cases accounts for this discrepancy; for part of the heat
developed is due to the induction-currents produced in the
electromagnet and its keeper by the motion of the keeper. The
quantity of electricity here set in motion is indeed the same
whether the keeper is loaded or not; but if the keeper is free, it
moves quicker than if it performs work, and therefore the in-
duction-currents in question have in the first case a shorter
duration than in the latter. The same quantity of electricity
performs its circulation in a shorter time when the keeper is free

* Phil. Mag. S. 4. vol. xxxi. p. 253.
† *Comptes Rendus,* vol. xlv. p. 56.

than when it is loaded.   Hence the intensity of the induction-current must be greater in the former case than in the latter case, though the entire quantity in circulation is the same in both cases.   But since the quantity of heat developed is proportional to the square of the intensity of the current, it may be readily shown that the quantity of heat excited by the induction-currents in the electromagnet and its keeper is greater if the keeper is free and therefore moves quicker, than if it performs mechanical work and its keeper therefore moves more slowly.   A similar behaviour is met with in the induction-currents which in both cases are formed in the path of the voltaic current.   The intervention of induction-currents is in this case so necessary for removing the discrepancy in question, that, if it had not been previously known, its existence might probably have been guessed from similar considerations.

2. Voltaic induction and the absorption of heat in chemical decomposition have long been known; and in the preceding we have endeavoured to show how intimately these phenomena are connected with an accurate conception of force and of work.   We will now pass over to a case in which the means have not hitherto been known which nature uses to remove the discrepancy between the demonstrated principle that the development of heat by a voltaic current depends upon the electromotive force and the resistance, and the axiomatic truth that if a force simultaneously brings about two actions, the sum of their quantitative values must be as great as the quantitative value of either of them if this alone is produced.

Such a case is the electric light which is formed when electricity passes through a gas from one solid conductor to another with development of heat and light.   It is a well-known fact that in this luminous arc material particles are detached by the current from one pole and transferred to the other.   The positive pole more especially suffers this disintegration, while the negative is less exposed to it.   But besides this purely mechanical work thus performed by the current, chemical decomposition may occur in the arc through the direct cooperation of the current.   If the formation of new chemical compounds is to take place there, this cannot be regarded as a direct and exclusive action of the current, but has at any rate partially its cause outside and independently of it.   As regards the chemical decompositions, the mechanical work which the current requires for their production has its mechanical thermal equivalent in the absorption of heat which thereby ensues.   With the purely mechanical disintegration of the poles the case is quite different.   No absorption of heat is connected with disintegration, but, on the contrary, a considerable production of heat.

Hence in the luminous arc the current performs a mechanical work which is not compensated by the absorption of heat which takes place there.

We assume a voltaic battery of given electromotive force and its poles connected by a solid conductor with a definite resistance. The quantity of heat which is then produced by the current in a given time is likewise determined. If now we assume that a part of the solid conductor is taken away, and that in its place there is a luminous arc between carbon points; suppose, further, that its resistance is as great as that of the piece taken away; by this exchange the entire resistance in the circuit is not altered. Yet the total quantity of heat produced by the current must be smaller than that which can be calculated from the electromotive force and the resistance; for now the current, along with the production of heat, performs the mechanical work necessary for detaching the material particles from the poles. This discrepancy can only be removed if the intensity of the current is diminished by so much that the diminution of heat thereby produced exactly corresponds to this mechanical work. But this mechanical work can only effect a diminution of the intensity in two ways—either by its acting in a manner similar to an increase of the resistance, or by giving rise to an electromotive force which sends a current in the opposite direction to the principal current. But now it is readily seen that if the requisite diminution of intensity is to be effected by an increase in the resistance due to the mechanical work, this increase must be of a different kind from an ordinary voltaic resistance. The resistance caused by the work must be of such a kind that it diminishes the intensity without the current producing a corresponding quantity of heat in overcoming it. Assuming for a moment that the resistance is of the ordinary kind and that we designate it by m, the resistance in the entire circuit by M; the entire resistance while the voltaic arc lasts is $M + m$. If now the voltaic arc be removed and the resistance made equal to $M + m$ by interposing a solid conductor, since the electromotive force remains unchanged, the same quantity of heat must be obtained as if the luminous arc existed; and we cannot get out of the dilemma which the assumption of an increase in the resistance was intended to remove. Hence the resistance in question, if its object is to be attained, must be of such a character that it brings about a diminution in the intensity of the current without causing a development of heat when the current passes through it or overcomes it. Such resistances are not yet known, and the one in question would be a resistance of a new kind. How the required lowering of the intensity is really brought about may be best seen from the three previously men-

tioned cases, in which we know accurately what takes place. If the current passes through a liquid chemical compound, a chemical decomposition is set up in it. The work which the current exerts in producing this decomposition, from our present point of view, is quite analogous to the mechanical work required in the voltaic arc for disintegrating the polar wires. In the first case it is the attraction between different substances, and in the latter the attraction between particles of the same kind, which has to be overcome by the current in order to effect a separation ; but this difference between the forces overcome in the two cases can have no influence on the reflex action of the work on the current itself. Now we know for certain that the work of chemical decomposition performed by the current does *not* diminish the intensity in such a manner as to increase the resistance; for this chemical work is quite compensated by the absorption of heat which takes place in decomposition. We must thence conclude that the disintegration of the pole-surfaces in the luminous arc has also in this case no influence on the magnitude of the resistance. Passing to the two cases mentioned in which induction takes place, we find that the work produced by the current is compensated by electromotive forces, and not by the intensity being lessened by an increase in the resistance. Since, then, in the three cases mentioned, the mechanical work performed by the current is not compensated by the intensity being lessened owing to increased resistance, we must assume that the deportment in the fourth case must be the same, since we can assign no valid reason for the contrary. In addition to this, there is another reason, which must not be left out of sight. It is known, from another branch of electrical science[*], that the disintegration of solids, by breaking, filing, scraping, &c., frequently developes electricity. This would doubtless always be the case if it were possible to remove the parts separated so quickly from one another that the separated electricities had no time to recombine. By the whole of this we are led to the conclusion *that in the electric light, by the mechanical disintegration of the solid poles, an electromotive force is produced, which sends a current in the opposite direction to the principal current.*

We shall now show how this conclusion agrees with experiment.

3. If an electromotive force is present in the voltaic arc, it must of course remain constant and unchanged as long as the electromotive force of the battery, the intensity of the current, and the resistance remain unchanged. It must therefore be independent of the length of the arc, provided that, when the arc is lengthened, so much of the other resistance is taken out that the

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[*] Riess, *Die Lehre von der Reibungselectricität,* vol. ii. p. 400.

entire resistance of the current remains the same as before.   If these conditions are fulfilled, the electromotive force in the voltaic arc is the same, whether its length be greater or less.   The force in question sends a current in an opposite direction to the principal current, and therefore diminishes the total intensity.   It acts in diminishing the intensity in the same manner as an interposed resistance.   It is clear, on the other hand, that the real resistance in the luminous arc must, under circumstances otherwise similar, increase with its length.   If, then, the resistance in the arc be measured, it will be found that this consists of two parts, one of which is independent of the length of the arc, and the other increases with it.   If the first resistance be denoted by a, and the proper resistance in a luminous arc of the length of a division of the scale by b_1, the entire resistance measured in a luminous arc of this length is $=a+b_1$.   If the luminous arc has a length of two divisions and the mean resistance in each is called b_2, the entire resistance in this arc is $=a+2b_2$.   In an arc of the length of three divisions of the scale it is $=a+3b_3$, and so forth.   The subsequent experiments show that a has a very considerable value, and that b_1, b_2, b_3, &c. are equally great.

The battery used was one of Bunsen's with carbon in nitric acid. As rheostat, a wooden trough was used, coated on the inside with asphalt.   It was 440 millims. in length by 148 in breadth and the same in depth, and was partly filled with solution of blue vitriol. In the trough were two copper plates of the same breadth as it, and reaching to the bottom.   One of these was fixed; the other could be moved parallel to it, and the distance between the two read off on the upper edge of the trough, which for this purpose was graduated.   The current came into the solution through one plate and out through the other.   In order to avoid the influence of polarization on the accuracy of the measurements, a greater or a smaller part of the rheostat was always brought into the conduction.   The current could be measured by a tangent-compass and be inverted by a commutator.   As in these experiments only currents of considerable strength were applicable, metal wires could not be used as rheostat, because they would have been very strongly heated, and thereby have had their resistance altered.

The poles between which the luminous arc was formed were placed in Foucault's apparatus for producing constant electric light.   In most experiments, however, the apparatus was only used as a pole-holder, and the definite distance between the points produced by moving one of the pole-points by the hand[*].

* Professor Stenberg, of the Carolinian Medico-Chirurgical Institute, who took part in all these experiments, determined the length of the lu-

During the experiments the apparatus was placed in the lamp belonging to it. The length of the luminous arc was not directly determined by measuring the distance between the points, but, by means of a lens introduced into the lamp, a magnified image was taken, which was projected on a scale on the opposite wall of the room. The distance between the parallel divisions of the scale was 10 millims. The glass lens magnified twenty-five times. Each division of the scale corresponded to about 0·4 millim. To make the image of the luminous arc very distinct, most of the daylight was excluded from the working-room.

First set of Experiments.

4. The battery consisted of seventy-six elements, the pole-points were of hard carbon, externally of the same kind as that of the battery. When only 0·6 inch of the rheostat was inserted in the circuit and the carbon points were in contact, the deflection of the tangent-compass amounted to 63° 30′; and when 8·4 inches were inserted, 51° 5′. We obtain from this 11·994 units of resistance as the resistance M *outside* of the rheostat. After the termination of the experiment the tangent-compass showed 64° in the first, and 52° 10′ in the latter case. From this we obtain M = 12·577; and the mean value for M during the experiments was 12·285 units of resistance.

Experiment I. When an electric light of the length of 5 divisions of the scale was formed, and 0·6 inch of the rheostat interposed in the circuit, the intensity of the current was = Tg. 51° 5′. When the carbon points were thereupon brought in contact and pressed hard against each other, 8·4 inches of the rheostat had to be introduced into the circuit in order to bring the tangent-compass to the angle of deflection mentioned. Thus the total resistance in this voltaic arc was 8·4−0·6 = 7·8 units. With the same intensity the following results were obtained for shorter arcs:—

Length of the arc = 4 parts of the scale.   Resistance = 7·6
    ,,   ,,   3   ,,   ,,   ,,   7·3
    ,,   ,,   2   ,,   ,,   ,,   7·1
    ,,   ,,   1   ,,   ,,   ,,   6·9

We thus obtain $a+5b_5=7\cdot8$, $a+4b_4=7\cdot6$, $a+3b_3=7\cdot3$, $a+2b_2=7\cdot1$, and $a+b_1=6\cdot9$. For each increase of one division of the scale in the length of the arc, the resistance is increased by 0·2 unit. We may thus conclude that $b_5=b_4=b_3=b_2=b_1$, and $a=6\cdot7$.

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minous arc by altering the position of the points, while I read off the intensity on the galvanometer. I avail myself of this opportunity of heartily thanking Professor Stenberg.

The electromotive force which is produced in the luminous arc diminishes the intensity by an amount corresponding to an interposed resistance of 6·7 units of resistance. From this we may easily calculate the magnitude of this opposing force expressed as electromotive force of the battery. If the latter be denoted by E and the electromotive force in the luminous arc by D, we have

$$\frac{E}{12{\cdot}285 + 8{\cdot}4 = 20{\cdot}685} = \frac{E - D}{20{\cdot}685 - 6{\cdot}7 = 13{\cdot}985},$$

from which we obtain D = 0·3239 E.

Experiment II. When the resistance M was increased to 14·176 units, and 11·0 units of the rheostat were interposed in the circuit, the intensity was = Tg. 45° 30'. The following results were obtained with this intensity :—

Length of the arc = 3 divisions. Resistance = 10·4
    „   „   2 „   „   = 9·8
    „   „   1 „   „   = 9·2

For this intensity we have thus $a + 3b = 10{\cdot}4$, $a + 2b = 9{\cdot}8$, and $a + b = 9{\cdot}2$, from which $a = 8{\cdot}6$ and $b = 0{\cdot}6$.

Calculating D in the same manner as in the preceding experiment, we have

$$D = 0{\cdot}3416 \ E.$$

Experiment III. In this experiment M was made = 21·29 units. When 13·5 inches of the rheostat was inserted in addition, the tangent-compass indicated 36° 22' in the mean. The entire length of the rheostat was 13·5 inches ; so that, retaining the value mentioned for M, the intensity could not have been made smaller by means of the rheostat. When the length of the luminous arc amounted to 2 divisions, the deflection of the galvanometer was 33° 40'. From this the resistance in the luminous arc may be readily calculated. For we obtain :—

Length of the arc = 2 divisions. Resistance = 16·66
    „   „   = 1 „   „   = 14·76

We thus obtain, since the intensity is = Tg. 33° 40', $a + 2b = 16{\cdot}66$ and $a + b = 14{\cdot}76$, from which $a = 12{\cdot}86$ and $b = 1{\cdot}9$.

From this we obtain, in the same manner as the first experiment,

$$D = 0{\cdot}3336 \ E.$$

5. *It results from the preceding experiments that the electromotive force D in the luminous arc is independent of the intensity of the current, and that the essential resistance of the luminous arc is proportional to its length, and increases as the intensity diminishes.*

That D should be independent of the intensity, at first sight seems unexpected; closer consideration shows, however, that this entirely agrees with other properties of the voltaic current which are connected with it. The work which the current exerts in disintegrating the points of the poles is measured by the diminution in the total heat developed by the current which results from the electromotive force D caused by the disintegration. If E is the electromotive force, and L the resistance for a certain intensity when there is no luminous arc, $\frac{E}{L}$ is the intensity, and $\frac{E^2}{L}$ the entire quantity of heat developed by the current. If, on the contrary, a luminous arc is formed, and L expresses the entire resistance, $\frac{E-D}{L}$ is the intensity, and $\frac{(E-D)^2}{L}$ the quantity of heat produced. The work performed by the current in the luminous arc has its equivalent in the difference between these two quantities, or $\frac{E^2-(E-D)^2}{L} = \frac{D(2E-D)}{L}$. If the resistance is L' and the intensity therefore different, the same equivalent becomes $\frac{D(2E-D)}{L'}$. If the mechanical work in the first case is A and in the latter A', we have thus $A : A' = L' : L$. But the resistances L' and L are inversely as the intensities. It follows thence, finally, *that the work performed by the current in the luminous arc is proportional to the intensity so long as the electromotive force of the battery remains constant.* The work which the current performs in the production of heat obeys the same law. The heat produced is proportional to $E \cdot \frac{E}{L'}$; and therefore, if E is constant proportional to the intensity, this equivalence between the two cases, as is easily seen, would not occur if D were not independent of the intensity.

Second Series of Experiments.

6. This series was undertaken in order to ascertain whether and in what manner D could be dependent on the electromotive force of the battery. Hence the experiments were made with a different number of elements. Since new carbon points were used in these experiments, which in hardness and other properties were different from those previously used, and since, moreover, the solution of sulphate of copper used in the rheostat might have altered in the interval between the two series, they cannot be considered directly comparable.

Experiment IV. The battery consisted of seventy-nine elements.

When 0·6 inch of the rheostat was interposed in the circuit and the carbon points pressed hard against each other, so that the contact was complete, the deflection of the compass amounted to 60° 35′. When 13·5 units of the rheostat were interposed, the deflection was 42° 55′. From this we can calculate that the total resistance external to the rheostat, or M, amounted to 13·62 units of resistance. Taking as unity the electromotive force which for the resistance 1 produces a deflection of 45° on the tangent-compass, the electromotive force of the battery or E = 25·22.

When 0·6 inch of the rheostat was interposed in the circuit, and the luminous arc was 4 divisions of the scale in length, the tangent-compass remained at 48°·5. When 9 inches was therefore interposed and the carbon points pressed to contact, the same number of degrees was obtained. The resistance in a luminous arc of the length of four divisions was thus = 8·4.

Retaining the same intensity of current, the following results were obtained for shorter arcs :—

Length of the arc = 3 divisions. Resistance = 7·8
    ,,   ,,   = 2   ,,   ,,   = 7·2
    ,,   ,,   = 1   ,,   ,,   = 6·6

From which is obtained $a = 6·0$ and $b = 0·6$.

If, therefore, D be calculated in the same manner as before, by the equation

$$\frac{E}{13·62 + 9·0 = 22·62} = \frac{E - D}{22·62 - 6·0 = 16·62},$$

we obtain

$$D = 0·2652 \times E = 6·69.$$

Experiment V. Twenty-four of the elements were detached from the battery, so that it only consisted of fifty-five. When 0·6 inch of the rheostat was interposed in the circuit and the points were in contact, the needle of the tangent-compass remained at 63° 32′; and when 13·5 inches was interposed, at 38° 59′. From this it may be calculated that the entire resistance *outside* the rheostat, or M, = 8·104, and E′ = 17·483.

When 0·6 inch of the rheostat was interposed in the circuit, and the length of the luminous arc was 2 divisions, the tangent-compass indicated 43° 20′; and after 10·2 inches had been brought into the circuit and the carbon points were in contact, the same number of degrees was obtained. From this we get

Length of the arc = 2 divisions. Resistance = 9·6.

We have now, therefore, $a = 7·2$ and $b = 1·2$. Calculating D in the same manner as before, we obtain

$$D = 0·3934 \times E′ = 6·877.$$

Both these experiments lead, therefore, to the result that D is also independent of the electromotive force of the battery.

Third Series of Experiments.

7. In this series iron was used for the pole-points. It was observed that the points became strongly oxidized, by which the conduction in the arc was less and the intensity diminished, so that it was difficult to obtain an accurate and trustworthy measure for the resistance of the luminous arc. Between two successive experiments the oxide had to be removed with a file.

The following numbers were obtained before a thick coating of oxide had time to form.

Experiment VI. The intensity was = Tg. 54° 15′.

Length of the luminous arc	=4 divisions.	Resistance	=3·4
,, ,,	=2	,, ,,	=3·1
,, ,,	=2	,, ,,	=2·8
,, ,,	=1	,, ,,	=2·45

Experiment VII. The intensity was = Tg. 56° 25′.

| Length of the luminous arc | =4 divisions. | Resistance | =3·3 |
| ,, ,, | =1 | ,, ,, | =2·4 |

The battery in both these experiments consisted of fifty Bunsen's elements.

Fourth Series of Experiments.

In this series carbon points were again used, yet of a different kind to the former ones. The rheostat was emptied, cleaned, and filled again with solution of sulphate of copper.

Experiment VIII. The battery consisted of seventy-seven elements. When 0·6 inch of the rheostat was interposed in the circuit, the needle stood at 63° 43′; and when thereupon thirteen units were interposed, at 43° 53′. From this are calculated M = 10·62 and E = 22·73. When 0·6 inch only of the rheostat was in the circuit, and the length of the arc was = 4 divisions, the resistance was = 6·7.

For the same intensity there was obtained :—

Length of the arc	=3 divisions.	Resistance	=6·2
,,	=2	,, ,,	=5·9
,,	=1	,, ,,	=5·4

Experiment IX. In this experiment twenty elements were taken away, so that the battery only consisted of fifty-seven. When there was 0·6 inch of the rheostat in the circuit, the deflection on

the galvanometer amounted to 62° 6'; and when 13 units were interposed, 37° 44'. From this are obtained $M' = 8.425$, and $E = 15.91$. When 0.6 inch of the rheostat was in the circuit, the following result was obtained:—

Length of the arc = 2 divisions. Resistance $= 8.9$;

and for the same intensity,

Length of the arc = 1 division. Resistance $= 8.1$.

From experiment VIII. we get $D = 0.279 \times E = 6.34$, and from Exp. IX. $D = 0.407 \times E' = 6.48$. This series leads, therefore, to the same result as Series 2, namely that D is independent of the electromotive force of the battery.

Fifth Series of Experiments.

8. The magnitude of the development of heat in the luminous arc depends upon the intensity of the current and the resistance of the arc, and is proportional to the latter. Now, since the actual resistance is not greater than the preceding experiments indicate, and it only amounts to a small fraction of that which has hitherto been assumed, it might perhaps be doubted whether this resistance is great enough to explain the formation of the high temperature which takes place in the luminous arc. The following experiments were undertaken with the view of investigating this.

The platinum wire used in my previous experiments on galvanic expansion (1150 millims. in length and 0.542 in diameter) indicated a constant expansion of 138 divisions when a current passed through it whose intensity was = Tg. 43° 21'. In the first second after the cessation of the current the wire cooled so that it shortened by 12.94 divisions (almost exactly corresponding to 7° of temperature). Since a current of the strength in question was sufficient to keep the wire at a constant length, this current must have produced an increase in temperature in the wire of 7 degrees in each second, which corresponds to a development of 1.27 thermal unit, if the gramme is taken as unit of weight. The resistance of this wire was now measured with the rheostat used in Experiments VIII. and IX.; and it was found that it amounted to 0.35 unit of resistance—something less, therefore, than that of a luminous arc of the length of one division of the scale (0.4 millim.) in Experiment VIII. In this experiment, in which the intensity was considerably greater than in the experiment on galvanic expansion, more than 1.27 thermal unit was developed in each division of the luminous arc in one second. This quantity of heat (1.27 unit) is sufficient to raise the tempe-

rature in a piece of platinum wire of the length of 0·4 millim. to more than 2000 degrees, if this could happen without the wire melting or being changed into gas. It is thus evident that the resistance which, from what precedes, is actually present in the luminous arc is sufficient to explain the production of the high temperature which is observed there.

Sixth Series of Experiments.

9. When carbon points were used in the formation of the luminous arc, the intensity was not constant during a long time, but changed after short intervals. This was due to the circumstance that the luminous arc was not steady, but passed from one point to another on the carbon points; and this displacement was often accompanied by a crackling sound. The magnetic needle hence began to move, by which the reading off was rendered more difficult. Hence it not unfrequently happened that for a single observation a pretty long time was needed, because the reading-off had to be delayed until the needle was at rest. The experiment was made with several kinds of carbon; yet all presented this inconvenience, which only entirely disappeared when a couple of thick copper wires were used instead of charcoal points. The intensity was now constant, and only diminished as the distance between the wires was increased. The subsequent determinations furnish the result of the experiments made with the copper wires.

Experiment X. The battery consisted of seventy-six Bunsen's elements. When 4 inches of the rheostat was interposed, the tangent-compass indicated 54° 15′ in the mean; and when 13 inches was interposed, 40° 50′. From this are calculated $M = 10.82$ and $E = 20.58$. When 0·7 inch of the rheostat was thereupon interposed in the circuit and formed a luminous arc of six divisions, the magnetic needle remained at 53°. With this intensity the following results were obtained:—

Length of the arc	=6 divisions.	Resistance	=4·2
"	=4	"	"	=4·0
"	=2	"	"	=3·8
"	=1	"	"	=3·6

From this are obtained $a = 3.4$ and $b = 0.2$.

And by simple calculation we have

$$D = \frac{3.4\,E}{15.72} = 4.45.$$

Experiment XI. Twenty of the elements were removed from the battery, so that only fifty-six were at work. When 4 inches of the rheostat were interposed in the circuit, the intensity was

= Tg. 52° 29'; and when 13 inches was inserted, = Tg. 35° 42'. From this are obtained M' = 7·08, and E' = 14·43.

When 1·4 inch of the rheostat formed the resistance, and the luminous arc was six divisions long, the magnetic needle indicated 44° 30'. With this intensity the following results were obtained:—

Length of the arc = 6 divisions.   Resistance = 6·2
,,   ,,   4   ,,   ,,   = 5·9
,,   ,,   2   ,,   ,,   = 5·6

From this we obtain $a = 5·3$ and $b = 0·15$.

The electromotive force calculated from this is found to be

$$D = \frac{5·3\,E}{14·68} = 5·21.$$

As 4·45 and 5·21 are equal within the limits of possible errors of observation, we find from this series also that D is independent of the electromotive force of the element.

10. It follows from the above that D is smaller if copper is used for the pole-points than when they are formed of solid and hard carbon. This may arise from the circumstance that the copper before being detached is in a fused or half-fused condition, owing to which the work which the current performs in the disintegration is less. Experiments were also made with carbon of very porous structure; but, as no constant results could be obtained with them, I do not think them worth communicating. Yet they showed that with the less-dense kinds of carbon D was smaller. The experiments made with tin gave also a smaller value for D; but the results obtained with this metal were less certain, because the quantity of oxide of tin formed disturbed the steadiness of the light and caused irregularities in the intensity.

Since the two points have different temperatures, it was possible that a thermo-electric force might be at work in the luminous arc. Probably also the aqueous vapour in the air was decomposed by the voltaic current; and if the products of decomposition (hydrogen and oxygen) were deposited on the poles, this would give rise to a polarization current opposite in direction to the principal current. But even if both these sources of electricity are present in the luminous arc, they can only form an insignificant fraction of the above-found electromotive force D, even supposing the polarization to have reached its maximum intensity. To get rid of all polarization, the experiments would have had to be made either in a vacuum or in a gas which is not decomposed by the current.

XIII. *On the Integration of the General Linear Partial Differential Equation of the Second Order. By* R. Moon, *M.A., Honorary Fellow of Queen's College, Cambridge**.

I PROPOSE to show in the following paper that when the equation

$$0 = \mathrm{R}\frac{d^2z}{dx^2} + \mathrm{S}\frac{d^2z}{dx\,dy} + \mathrm{T}\frac{d^2z}{dy^2} + \mathrm{V} \quad . \quad . \quad . \quad (1)$$

is derivable from a single partial differential equation of the first order, such single equation will be of one or other of the three following forms, viz. :—

$$\text{I.} \quad q = f(xyzp),$$

where f satisfies both the equations

$$0 = f'(p) - m_1,$$

$$0 = m_2 f'(x) - f'(y) + (m_2 p - f)f'(z) - \left(\frac{\mathrm{V}}{\mathrm{T}}\right)_{q=f},$$

where m_1, m_2 are the roots of the equation

$$0 = \mathrm{T}_{q=f} \cdot m^2 + \mathrm{S}_{q=f} \cdot m + \mathrm{R}_{q=f}.$$

$$\text{II.} \quad q = f(xyz),$$

where we have simultaneously

$$0 = \mathrm{R}_{q=f},$$

$$0 = \mathrm{T}_{q=f} \cdot f'(y) + \mathrm{S}_{q=f} \cdot f'(x) + (\mathrm{T}_{q=f} \cdot f + \mathrm{S}_{q=f} \cdot p)f'(z) + \mathrm{V} \quad .$$

$$\text{III.} \quad p = f(xyz),$$

where we have simultaneously

$$0 = \mathrm{T}_{p=f},$$

$$0 = \mathrm{R}_{p=f} \cdot f'(x) + \mathrm{S}_{p=f} \cdot f'(y) + (\mathrm{R}_{p=f} \cdot f + \mathrm{S}_{p=f} \cdot q)f'(z) + \mathrm{V}_{p=f}.$$

I. Let definite values be assigned to any arbitrary functions which may be contained in the single equation of the first order from which (1) is derivable, so that it may be represented by

$$q = f(xyzp), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

unless indeed it do not contain q, a case hereafter to be considered.

Differentiating (2), we get

$$0 = \frac{d^2z}{dy^2} - f'(p)\frac{d^2z}{dx\,dy} - f_y, \quad . \quad . \quad . \quad (3)$$

$$0 = \frac{d^2z}{dx\,dy} - f'(p)\frac{d^2z}{dy^2} - f_x, \quad . \quad . \quad . \quad (4)$$

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* Communicated by the Author.

where f_x, f_y respectively denote the complete derivatives of f with respect to x and y, *taken on the assumption that* p *is constant.*

The two last equations embody *all* the relations between the partial differential coefficients $\dfrac{d^2z}{dx^2}$, $\dfrac{d^2z}{dp^2}$, $\dfrac{d^2z}{dx\,dy}$, and the variables x, y, z, p which are capable of being derived from (2).

But if we put f for q in (1), we shall have in the equation

$$0 = R_{q=f} \cdot \frac{d^2z}{dx^2} + S_{q=f} \cdot \frac{d^2z}{dx\,dy} + T_{q=f} \cdot \frac{d^2z}{dy^2} + V_{q=f}, \quad (5)$$

a relation between the same partial differential coefficients and variables which by hypothesis is derivable from (2). Hence the right side of (5) must be identical with

$$A\left\{ \frac{d^2z}{dy^2} - f'(p)\frac{d^2z}{dx\,dy} - f_y \right\} + B\left\{ \frac{d^2z}{dx\,dy} - f'(p)\frac{d^2z}{dx^2} - f_x \right\},$$

where A, B are functions of x, y, z, p; in order to which we must have

$$\left.\begin{aligned}
A &= T_{q=f}, \\
B - A\cdot f'(p) &= S_{q=f}, \\
-B\cdot f'(p) &= R_{q=f}, \\
Af_y + Bf_x &= -V_{q=f},
\end{aligned}\right\} \quad \dots \quad (5')$$

whence, eliminating A and B, we get

$$0 = T_{q=f} \cdot \overline{f'(p)}|^2 + S_{q=f} \cdot f'(p) + R_{q=f}, \quad \cdot \quad \cdot \quad (6)$$

$$0 = R_{q=f} \cdot f_x - (T_{q=f} \cdot f_y + V_{q=f}) f'(p). \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

Let m_1, m_2 be the values of $f'(p)$ given by (6); and putting m_1 for $f'(p)$ and dividing by $T_{q=f}$, (1) becomes

$$0 = m_1 m_2 f_x - \left\{ f_y + \left(\frac{V}{T}\right)_{q=f} \right\} m_1,$$

or

$$0 = m_2 f'(x) - f'(y) + (m_2 p - f) \cdot f'(z) - \left(\frac{V}{T}\right)_{q=f}. \quad \cdot \quad (8)$$

The function f must satisfy simultaneously (8) and also the equation

$$0 = f'(p) - m_1. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

As an illustration of the mode of procedure necessary to find f, take the case where $\dfrac{V}{T}$ is of the form $\alpha p + \beta q + \gamma z + \delta$, and all the coefficients R, S, T and α, β, γ, δ contain x and y only.

Integrating (9), we have

$$f(xyzp) = m_1 p + f_a(xyz).$$

Substituting this value of f in (8), and also the above value of $\dfrac{V}{T}$, and observing that

$$f'(x) = f_a'(x) + p \cdot \frac{dm_1}{dx},$$

$$f'(y) = f_a'(y) + p \cdot \frac{dm_1}{dy},$$

$$f'(z) = f_a'(z),$$

we shall get

$$0 = m_2 f_a'(x) - f_a'(y) + \overline{(m_2 - m_1 \cdot p - f_x)} f'(z) + \left(m_2 \frac{dm_1}{dx} - \frac{dm_1}{dy} \right) p$$
$$- (\alpha + m_1 \beta) p - \beta \cdot f_a - \gamma \cdot z - \delta \,;$$

and since f involves x, y, z only, the terms involving p must separately $= 0$. Hence we shall have simultaneously

$$0 = m_2 f_a'(x) - f_a'(y) - f_a \cdot f_a'(z) - \beta \cdot f_a - \gamma z - \delta, \qquad . \quad (10)$$

$$\left. 0 = (m_2 - m_1) f_a'(z) - (\alpha + m_1 \beta) + m_2 \frac{dm_1}{dx} - \frac{dm_1}{dy}, \right\} \quad . \quad (11)$$

both of which must be satisfied by f_a.

Integrating (11), we get

$$f_a(xyz) = \frac{1}{m_2 - m_1} \left\{ \alpha + m_1 \beta + \frac{dm_1}{dy} - m_2 \frac{dm_1}{dx} \right\} z + f_b(xy)$$
$$= \mu z + f_b(x, y) \text{ suppose.}$$

Substituting this in (10), observing that

$$f_a'(x) = f_b'(x) + \frac{d\mu}{dx} \cdot z,$$

$$f_a'(y) = f_b'(y) + \frac{d\mu}{dy} \cdot z,$$

$$f_a'(z) = \qquad \mu,$$

we shall get

$$0 = m_2 f_b'(x) - f_b'(y) + \left(m_2 \frac{d\mu}{dx} - \frac{d\mu}{dy} \right) z - (\mu z + f_b)(\mu + \beta) - \gamma z - \delta.$$

And since f_b contains x and y only, the terms involving z must vanish; hence we must have simultaneously

$$0 = m_2 f_b'(x) - f_b'(y) - (\mu + \beta) f_b - \delta,$$

$$0 = m_2 \frac{d\mu}{dx} - \frac{d\mu}{dy} - \mu(\mu + \beta) - \gamma,$$

the last of which is an equation of condition requiring to be satisfied by the coefficients of (1), in order that it may be capable of being derived from a single equation of the form (I.).

When the condition is satisfied, we have for the determination of f_b a partial differential equation of the first order involving two independent variables; and substituting this in the equation

$$0 = q - m_1 p - \mu z - f_b,$$

we shall have the first integral of (1).

II. The equations (5′) hold always when the partial differential equation of the first order from which (1) is derivable contains q; but the results above derived from those equations fail if $f'(p) = 0$, since in that case the foregoing elimination of A and B from the equations (5) becomes illusory.

In this case the equations (5′) become

$$A = T_{q=f},$$
$$B = S_{q=f},$$
$$0 = R_{q=f},$$
$$A f_y + B f_x = - V_{q=f}.$$

So that if (1) be derivable from a single partial differential equation of the first order which does not contain p, such equation must be of the form

$$q = f(xyz),$$

where we have simultaneously

$$0 = R_{q=f},$$
$$0 = T_{q=f} \cdot f'(y) + S_{q=f} \cdot f'(x) + (T_{q=f} \cdot f + S_{q=f} \cdot p) f'(z) + V_{q=f}.$$

If we have

$$V = Pp + Qq + Nz + M,$$

where R, S, T, P, Q, M, N are functions of x and y only, the above become

$$0 = R,$$
$$0 = T \cdot f'(y) + S \cdot f'(x) + (T \cdot f + S \cdot p) f'(z) + Pp + Qq + Nz + M; \quad (12)$$

and since f does not contain p, the terms in this equation which involve p must vanish separately. Hence we must have simultaneously

$$0 = T \cdot f'(y) + S \cdot f'(x) + \overline{T \cdot f'(z) + Q} \cdot f + Nz + M, \quad (13)$$
$$0 = S \cdot f'(z) + P. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Integrating (13), we get

$$f(xyz) = - \frac{P}{S} z + f_a(x, y);$$

and substituting this in (12), observing that

$$f'(y) = f_a'(y) - \frac{d}{dy}\left(\frac{P}{S}\right) \cdot z,$$

$$f'(x) = f_a'(x) - \frac{d}{dx}\left(\frac{P}{S}\right) \cdot z,$$

$$f'(z) = \qquad -\frac{P}{S},$$

we get

$$0 = T \cdot f_a'(y) + S \cdot f_a'(x) - \left\{ T \cdot \frac{d}{dy}\left(\frac{P}{S}\right) + S \cdot \frac{d}{dx}\left(\frac{P}{S}\right) \right\} z$$

$$+ \left(Q - \frac{PT}{S}\right)\left(f_a - \frac{P}{S} \cdot z\right) + Nz + M.$$

Hence, equating to zero the coefficient of z, since f contains x and y only, we must have simultaneously

$$0 = T \cdot f_a'(y) + S \cdot f_a'(x) + \left(Q - \frac{P}{S} T\right) \cdot f_a + M, \quad . \quad (15)$$

$$0 = T \cdot \frac{d}{dy}\left(\frac{P}{S}\right) + S \cdot \frac{d}{dx}\left(\frac{P}{S}\right) + \left(Q - \frac{P}{S} T\right) \cdot \frac{P}{S} + N. \quad (16)$$

And, finally, in order that the equation

$$0 = Rr + Ss + Tt + Pp + Qq + Nz + M$$

(where R, S, T, P, Q, M, N are functions of x and y only) **may be derivable from a single partial differential equation of the first order not containing** p, we must have satisfied *two* conditions. First, we must have $R = 0$; second, the other coefficients of (1) must satisfy (15). When these are satisfied, the required first integral will be

$$0 = q + \frac{P}{S} z + f_a(x, y),$$

where f_a is determined by (14).

The mode of treatment when the equation of the first order from which (1) is derivable does not contain q is, *mutatis mutandis,* precisely similar.

6 New Square, Lincoln's Inn,
    January 7, 1868.

XIV. *Observations on the Humming Sound produced on Mountains by Electricity. By* M. Henri de Saussure*.

ON the 22nd of June, 1865, leaving Saint Moritz (Grisons), I made the ascent of the Piz Surley, a mountain composed of crystalline rocks, of which the somewhat conical summit attains the height of about 3200 metres. During the preceding days the wind had blown steadily from the north, but on the 22nd it became variable, and the sky charged with scattered clouds. Towards midday these clouds increased in number and collected together over the highest peaks, elsewhere remaining so high that they did not hide the greater number of the spires and summits of the Engadine, on which soon fell some local showers. Their appearance, that of dust-like vapours, semi-transparent, made us think that they were but showers of snow or frozen sleet (*grésil*). Indeed, about 1 o'clock in the afternoon, we were ourselves overtaken by a fine hail thinly scattered, at the same time that similar showers enveloped the greater part of the spires of such rocks as the Piz Ot, Piz Languard, &c., and the snowy tops of the Bernina, and that a heavy fall of rain poured down on the valley of Saint Moritz. The cold increased ; and at half-past 1, when we had reached the summit of the Piz Surley, the sleet becoming more abundant, we disposed ourselves to take our repast, and laid our alpenstocks against a little cairn of dry stones which crowns the summit of the mountain. Almost at the same instant I felt at my back, in the left shoulder, a very acute pain like that produced by a pin lightly pressed into the flesh ; and when I put my hand there, without finding anything, a similar pain was felt in the right shoulder. Supposing my cloth overcoat to contain pins, I threw it off, but, far from finding myself relieved, I found that the pains increased, extending from one shoulder to the other across the whole back. They were accompanied by pricking sensations and sharp shooting pains, such as a wasp crawling over my skin and covering me with stings might produce. Taking off my second coat, I found nothing which could wound the flesh. The pain, which was continuous, took then the character of a burn. Without thinking more about it, I fancied, without being able to explain it, that my flannel waistcoat had taken fire, and was about to throw off the rest of my clothes, when my attention was arrested by a sound recalling the reverberations of a diapason. It came from our sticks, which, resting against the rock, sang loudly, emitting a sound like a kettle the water in which is about to boil. All this may have lasted four or five minutes.

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* Translated from the *Bibliothèque Universelle* for January 15, 1868.

I understood at once that my sensations were from a strong flow of electricity taking place from the summit of the mountain. Some improvised experiments produced no spark from our sticks, nor light perceptible by day; they vibrated strongly in the hand, and gave out a very pronounced sound; whether held vertically, the point upwards or downwards, or, on the other hand, horizontally, the vibrations remained identical, but no sound escaped from the soil.   The sky had become grey over its whole extent, though unequally charged with clouds.   Some minutes afterwards I felt my hair and beard stand out, causing me to feel a sensation like that resulting from a razor passed dry over the bristles. A young Frenchman who was with me cried out that he felt the hair of his moustache growing, and that strong currents were flowing from the tips of his ears.   Raising my hand, I felt currents no less strong flow off from the fingers.   Briefly, strong currents of electricity flowed from our staves, clothes, from our ears, hair, and all salient parts of our bodies. A single thunderclap was heard in the distance to the westward.   We left the summit in some haste and descended about a hundred metres. The further we advanced the less strongly our sticks vibrated, and we stopped when the sound had become too weak to be perceived except on bringing them close to the ear. The pain in the back ceased from the first step in our descent, but I still retained a vague feeling of it. Ten minutes after the first a second thunderclap was heard again to the westward and very distant; and these were the only ones.   No flash was seen.   Half an hour after leaving the summit the sleet had ceased, the clouds broke, and in two hours and a half we reached anew the summit of the Piz Surley to find there the sun.   We judged that the same phenomenon must have been produced on all the spires formed by needle-pointed rocks; for all, like that we were on, were surrounded by vortices of sleet: in the rest of the sky no condensation was produced, and the great snowy tops of the Bernina, to which were attached masses of cloud, appeared also free from the sleet. But the same day a violent storm broke out in the Bernese Alps, where an Englishwoman was killed.   On the horizon divers peaks, especially the sharp ones, were surrounded by hailshowers, even when the sky began to grow clear in all directions.

I was witness to another case of flowing of electricity from the summits of mountains when I visited, some years ago, the Nevado de Toluca in Mexico; but there the phenomenon had more intensity, as one may well understand, as it took place within the tropics, at a height of about 4500 metres.   Permit me here to repeat what I have elsewhere related.

In the month of August 1856 I made, with M. Peyrot, the ascent of the Nevado de Toluca.   We were in the height of

the rainy season, and it was almost imprudent to attempt the expedition at that time. We reached the summit without the sky appearing threatening, although we saw some cumuli floating about, and fogs for a moment skimmed close over the spires which crown the mountain. We seated ourselves at the edge of the crater to recover our strength and enjoy the grand view which was spread below us. From the top of the slope we looked down into that vast amphitheatre whose hearth, long cold, is now filled by two little lakes, towards which we made ready to descend. A cold and disagreeable wind blew up from the gulf; and while we took our scanty meal we saw a thick cloud penetrate to the crater by its south-eastern opening and mount towards us, creeping up the walls of the amphitheatre. We were soon enveloped in an ice-cold fog. Surprised by that threatening symptom, we saw that we had not a moment to lose if we were to visit the crater; and I began to descend across the rubbish which conducts to the depth of the amphitheatre. But scarcely had I reached halfway, when the storm, breaking out with astonishing suddenness, obliged me to remount as soon as possible to my point of departure. It was at first fine rain, then a little very fine hail driven by violent wind. In an instant the mountain was whitened, and the cold became intense. The thunder, which was at first intermittent, now rolled almost uninterruptedly and with frightful violence, above all when it arose from the amphitheatre of the crater, where I saw the flash of the lightning often fall. Without any shelter, in the midst of naked rocks, without even a block to cower under, our only resource was to sit down on the ground, turning our backs to the hail. After a short time the cold became insupportable, and, with fear of the tempest, drove us from the summit, though we had not finished our observations.

While we were hastily descending the rocks forming the summit of the Nevado, rain for an instant succeeded the sleet. As we were threading a little stony ravine formed by ancient runs of trachyte, and where vegetation begins, the storm appeared to grow calm for an instant, the claps of thunder ceased, or grew distant, and we saw a dark cloud approach; it passed over us, enveloping us, *and was accompanied with frozen sleet.* Soon we saw the hairs of our Indians move as though about to stand up, and we felt various electrical sensations at the beard and at the ears. Next we heard a deep indefinable sound, at first weak though general, but soon stronger and very distinct. It was a universal rattling, as though all the small stones on the mountain were being shaken together. The terrified Indians in their conversation gave free course to their superstition; and it is true that the clamour which then reigned in the moun-

tain was something disquieting. This phenomenon lasted some five or six minutes; soon the rain and the thunder recommenced anew. When we had reached the upper limits of the forests the storm became more endurable, though there fell one of those diluvial rains characteristic of the hot season within the tropics. M. F. Craveri, an Italian physician established at Mexico, who had made the ascent of the Nevado de Toluca before me *at the commencement of the rainy season*, told me that he had been witness of the same facts, which he remembered with terror. The electrical phenomena were yet more violent. On the 19th of May, 1845, that traveller ascended the Nevado de Toluca by the south-east side, starting from Tenango, and descended by the north-west slope on Toluca. The south-west side of the mountain was free from snow at that season.

The electrical phenomenon was brought on suddenly by a cloud coming from the west, and which perhaps had been generated on the snow-fields of that slope. Scarcely were the travellers enveloped in it ere they felt the sensation electricity produces; and this was almost immediately followed by a dull sound. They felt at all their extremities, at the fingers, nose, and ears, confused electrical currents. The fear which seized them, then in the midst of those lofty solitudes, made them immediately commence the descent with hasty steps. The thunder did not yet growl; but at the end of five minutes *there fell a snow like rice*, and, the cloud communicating its electricity to the soil, there arose from it the same sound that I have before described. This sound was very loud, and appeared general over the mountain. The long hair of the Indians became stiff and erect, giving an enormous size to the head of these people. The sight of this phenomenon added to the panic of those who had expected pleasure from this expedition. The so singular sound which is heard in the rocks of mountains at the moment of the electrical phenomenon deserves to be studied by competent physicists. It resembles the taps which little pebbles produce when they knock together as they are alternately attracted and repelled by electricity. But it seems certain to me that it arises from a kind of crepitation or crackling of the electricity which escapes from the rough points of the rocky soil.

A third observation of the same kind is due to M. Craveri, who was surprised by the same kind of storm near the summit of Popocatepetl, on the 15th of September 1855, with this difference, that, the scene taking place on snow-fields, the sound of crackling of the soil was not produced.

Here are facts bearing on the point that have come to my knowledge :—

In 1767 H. B. de Saussure visited the summit of the Brévent

in company with Pictet and Jalabert*. The travellers were then electrified to such an extent that, on stretching out their hands, they felt pricking sensations at the end of their fingers; the electricity escaped thence with a certain vibration; soon sparks could be got from the button of some gold lace which was round the hat of one of the party, as well as from the iron point of a mountain-staff. These effects were attributed to a great storm-cloud which occupied the middle region of Mont Blanc, and stretched itself, little by little, above the Brévent. At 80 feet below the top of the mountain the electricity was no longer felt. The storm growled around Mont Blanc, but on the Brévent there fell but one slight rain-shower of short duration, and the storm dispersed.

It is easy, by this account, to see that the storm did not reign over the Brévent at the moment of observation, since there fell no rain; but the electricity discharged itself in a continuous current from the summit of the mountain.

In July 1863, Mr. Spence Watson, visiting the Jungfrau with some guides, was overtaken by a hurricane accompanied by hail and snow. The staves began to *sing*; the travellers felt sensations of heat† in different parts of their bodies, above all in the head; and their hair stood erect. A guide took off his hat, saying that his head was on fire; a veil kept itself stretched out in the air. There escaped also electrical currents from the ends of the travellers' fingers. The thunder-claps (in the distance, for there was no flash visible) interrupted for an instant the phenomena: at last they felt some shocks, and Mr. Watson had the right arm paralyzed for some minutes; he continued to feel acute pain in the arm for many hours‡. During this time the snow fell with a hissing sound like hail§. But what is most remarkable is that the snow gave out a sound, a crackling, like that of a heavy shower of hail, evidently the analogue of that the ground gave out on the Nevado de Toluca above described. The phenomenon lasted twenty-five minutes. No other disagreeable result followed than the burning of the faces of the travellers as if they had been exposed to the sun on the snow.

Mr. Forbes, in passing by the St. Théodule, heard the singing of the staves; and in July 1856 M. Alizier, of Geneva, witnessed the same phenomenon near the summit of the Oldenhorn, under an overcast sky, where a storm was brewing which broke out an hour after, and *which was accompanied with hail*¶.

* *Voyage dans les Alpes*, vol. ii.
† This sensation of heat appears to me to have been the same kind of pain that I felt in the back.
‡ Alpine Journal, September 1863.
§ Probably *snow like rice*, frozen sleet (*grésil*).
¶ See *L'Echo des Alpes*, 1865, No. 4, notice by M. C.-M. Briquet,

We will not here speak of the storm during which Colonel Buchwalder and his aide were struck dead on the Sentis, because then a phenomenon was involved belonging rather to the nature of a discharge of lightning. But the lighting up of the rocks by night is probably due to a flow off of electricity from the highest points. M. Fournet cites on this point the beautiful illumination of the rocks of the Grands Mulets (Mont Blanc) observed by Mr. Blackwall on the night of the 11th of August, 1854, and which was accompanied by sparks. And, besides, the phenomenon of electricity seen on the lakes and very dry plains of elevated plateaus appears to us of the same nature. Finally, the curious fact of moving electricity coursing over the prairies observed by M. Quiquerez near Courtamon may be likened to a kind of lightning, a discharge in miniature, resulting from the electrified cloud brushing over the earth and discharging itself over its whole surface by a thousand sparks which were seen to course over the meadows. It is possible that these phenomena ought to be divided into several categories of which the causes are not the same. Some arise from statical tension, others from a series of discharges which have some analogy with lightning.

The phenomenon of the singing of the staves, or of the humming of the soil, constitutes yet another kind. It has been observed only on the summit or culminating ridges of hills; never, to my knowledge, in the plains or at the bottom of a valley. It supposes a continuous dynamical action, like a flow of electricity towards the clouds through the most salient terrestrial conductors, and is different from static tension or discharge by a spark.

Comparing the observations we have related, we remark several points they have in common.

1. The flow-off of electricity from the highest rocks on mountains takes place under an overcast sky with low clouds enveloping the summits or passing a little above them, but without electrical discharges taking place above the point where the continuous electrical flow occurs. It seems, then, that when this flow is able to occur, it lowers the electrical tension sufficiently to prevent the disruptive discharge occurring.

2. In every case observed the top of the mountain was enveloped in a shower of frozen sleet, which might make one suppose that the continuous flow of electricity from the ground to the clouds was not unconnected with its formation, and most likely also with the formation of hail.

" Sur les phénomènes électriques qui accompagnent les orages à de grandes altitudes," where these observations are collected and brought together. Geneva, 1865.

On the Piz Surley and the Nevado de Toluca there fell frozen sleet, or snow like rice; and on the Jungfrau the snow fell *hissing like hail,* which would seem to point to sleet rather than snow having fallen. No doubt we ought to take into consideration the higher temperature of the valley, where hail about to fall turns to rain; but we think that the cases we have just pointed out, of rain in the valleys and frozen sleet on the isolated mountain, show that the condensation is not one taking place over the whole sky according to the same law. Thus, in particular, during the observation of the 22nd of June, 1865, I saw on the horizon all the needles, though far distant from each other, enveloped in dirty sleet, which lasted for a very long time, whilst in the rest of the sky all condensation had ceased, and in the valley there fell but one heavy and short shower.

In the other cases the phenomenon which took place around the tops of the rocks was very different from that occurring in the valleys. Around the pyramids there were columns of frozen sleet, fine and very thinly scattered; in the valley, rain heavy and abundant, such as the thinly scattered sleet could not have produced if changed to rain. Around the pyramids by which the electricity flowed off, the condensation had then the special character of being less abundant, dust-like (fine frozen sleet), and was also more persistent than in the rest of the sky.

The electrical phenomenon which has here been described, and which we may call the humming of mountains (*bourdonnement des montagnes*), appears not to be uncommon though not very frequent at high altitudes. Among the guides and hunters whom I have questioned on the subject, some have never observed it, others have heard it some once or twice in their lives; but it is fair to add that it takes place on just those days when the threatening appearance of the sky keeps travellers from the highest peaks.

XV. *On the Dynamical Theory of Gases.*
By J. Clerk Maxwell, *F.R.S.L. & E.*[*]

THEORIES of the constitution of bodies suppose them either to be continuous and homogeneous, or to be composed of a finite number of distinct particles or molecules.

In certain applications of mathematics to physical questions, it is convenient to suppose bodies homogeneous in order to make the quantity of matter in each differential element a function of the coordinates, but I am not aware that any theory of this kind has been proposed to account for the different properties of

[*] From the Philosophical Transactions for 1867, Part I., having been read May 1, 1866.

bodies.   Indeed the properties of a body supposed to be a uniform *plenum* may be affirmed dogmatically, but cannot be explained mathematically.

Molecular theories suppose that all bodies, even when they appear to our senses homogeneous, consist of a multitude of particles or small parts, the mechanical relations of which constitute the properties of the bodies.   Those theories which suppose that the molecules are at rest relatively to the body may be called statical theories, and those which suppose the molecules to be in motion, even while the body is apparently at rest, may be called dynamical theories.

If we adopt a statical theory, and suppose the molecules of a body kept at rest in their positions of equilibrium by the action of forces in the directions of the lines joining their centres, we may determine the mechanical properties of a body so constructed, if distorted so that the displacement of each molecule is a function of its coordinates when in equilibrium.   It appears from the mathematical theory of bodies of this kind, that the forces called into play by a small change of form must always bear a fixed proportion to those excited by a small change of volume.

Now we know that in fluids the elasticity of form is evanescent, while that of volume is considerable.   Hence such theories will not apply to fluids.   In solid bodies the elasticity of form appears in many cases to be smaller in proportion to that of volume than the theory gives* ; so that we are forced to give up the theory of molecules whose displacements are functions of their coordinates when at rest, even in the case of solid bodies.

The theory of moving molecules, on the other hand, is not open to these objections.   The mathematical difficulties in applying the theory are considerable, and till they are surmounted we cannot fully decide on the applicability of the theory.   We are able, however, to explain a great variety of phenomena by the dynamical theory which have not been hitherto explained otherwise.

The dynamical theory supposes that the molecules of solid bodies oscillate about their positions of equilibrium, but do not travel from one position to another in the body.   In fluids the molecules are supposed to be constantly moving into new relative positions, so that the same molecule may travel from one part of the fluid to any other part.   In liquids the molecules are supposed to be always under the action of the forces due to neighbouring molecules throughout their course; but in gases the greater part of the path of each molecule is supposed to be

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* [In glass, according to Dr. Everett's second series of experiments (1866), the ratio of the elasticity of form to that of volume is greater than that given by the theory.   In brass and steel it is less.—March 7, 1867.]

sensibly rectilinear and beyond the sphere of sensible action of the neighbouring molecules.

I propose in this paper to apply this theory to the explanation of various properties of gases, and to show that, besides accounting for the relations of pressure, density, and temperature in a single gas, it affords a mechanical explanation of the known chemical relation between the density of a gas and its equivalent weight, commonly called the Law of Equivalent Volumes. It also explains the diffusion of one gas through another, the internal friction of a gas, and the conduction of heat through gases.

The opinion that the observed properties of visible bodies apparently at rest are due to the action of invisible molecules in rapid motion is to be found in Lucretius. In the exposition which he gives of the theories of Democritus as modified by Epicurus, he describes the invisible atoms as all moving downwards with equal velocities, which, at quite uncertain times and places, suffer an imperceptible change, just enough to allow of occasional collisions taking place between the atoms. These atoms he supposes to set small bodies in motion by an action of which we may form some conception by looking at the motes in a sunbeam. The language of Lucretius must of course be interpreted according to the physical ideas of his age ; but we need not wonder that it suggested to Le Sage the fundamental conception of his theory of gases, as well as his doctrine of ultramundane corpuscles.

Professor Clausius, to whom we owe the most extensive developments of the dynamical theory of gases, has given* a list of authors who have adopted or given countenance to any theory of invisible particles in motion. Of these, Daniel Bernoulli, in the tenth section of his ' Hydrodynamics,' distinctly explains the pressure of air by the impact of its particles on the sides of the vessel containing it.

Clausius also mentions a book entitled *"Deux Traités de Physique Mécanique, publiés par* Pierre Prevost, *comme simple Éditeur du premier et comme Auteur du second,"* Genève et Paris, 1818. The first memoir is by G. Le Sage, who explains gravity by the impact of "ultramundane corpuscles" on bodies. These corpuscles also set in motion the particles of light and various æthereal media, which in their turn act on the molecules of gases and keep up their motions. His theory of impact is faulty, but his explanation of the expansive force of gases is essentially the same as in the dynamical theory as it now stands. The second memoir, by Prevost, contains new applications of the prin-

* Poggendorff's *Annalen,* January 1862. Translated by G. C. Foster, B.A., Phil. Mag. June 1862.

ciples of Le Sage to gases and to light. A more extensive application of the theory of moving molecules was made by Herapath[*]. His theory of the collisions of perfectly hard bodies, such as he supposes the molecules to be, is faulty, inasmuch as it makes the result of impact depend on the absolute motion of the bodies, so that by experiments on such hard bodies (if we could get them) we might determine the absolute direction and velocity of the motion of the earth[†]. This author, however, has applied his theory to the numerical results of experiment in many cases; and his speculations are always ingenious, and often throw much real light on the questions treated. In particular, the theory of temperature and pressure in gases and the theory of diffusion are clearly pointed out.

Dr. Joule[‡] has also explained the pressure of gases by the impact of their molecules, and has calculated the velocity which they must have in order to produce the pressure observed in particular gases.

It is to Professor Clausius, of Zurich, that we owe the most complete dynamical theory of gases. His other researches on the general dynamical theory of heat are well known; and his memoirs " On the kind of Motion which we call Heat " are a complete exposition of the molecular theory adopted in this paper. After reading his investigation[§] of the distance described by each molecule between successive collisions, I published some propositions[||] on the motions and collisions of perfectly elastic spheres, and deduced several properties of gases, especially the law of equivalent volumes, and the nature of gaseous friction. I also gave a theory of diffusion of gases, which I now know to be erroneous; and there were several errors in my theory of the conduction of heat in gases, which M. Clausius has pointed out in an elaborate memoir on that subject[¶].

M. O. E. Meyer[**] has also investigated the theory of internal friction, on the hypothesis of hard elastic molecules.

In the present paper I propose to consider the molecules of a gas, not as elastic spheres of definite radius, but as small bodies or groups of smaller molecules repelling one another with a force whose direction always passes very nearly through the centres

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[*] Mathematical Physics &c., by John Herapath, Esq. 2 vols. London. Whittaker & Co., and Herapath's Railway Journal Office, 1847.

[†] Mathematical Physics &c., p. 134.

[‡] Some Remarks on Heat and the Constitution of Elastic Fluids, October 3, 1848.

[§] Phil. Mag. February 1859.

[||] " Illustrations of the Dynamical Theory of Gases," Phil. Mag. 1860, January and July.

[¶] Poggendorff, January 1862; Phil. Mag. June 1862.

[**] " Ueber die innere Reibung der Gase," Poggendorff, vol. cxxv. 1865.

of gravity of the molecules, and whose magnitude is represented very nearly by some function of the distance of the centres of gravity. I have made this modification of the theory in consequence of the results of my experiments on the viscosity of air at different temperatures, and I have deduced from these experiments that the repulsion is inversely as the *fifth* power of the distance.

If we suppose an imaginary plane drawn through a vessel containing a great number of such molecules in motion, then a great many molecules will cross the plane in either direction. The excess of the mass of those which traverse the plane in the positive direction over that of those which traverse it in the negative direction, gives a measure of the flow of gas through the plane in the positive direction.

If the plane be made to move with such a velocity that there is no excess of flow of molecules in one direction through it, then the velocity of the plane is the mean velocity of the gas resolved normal to the plane.

There will still be molecules moving in both directions through the plane, and carrying with them a certain amount of momentum into the portion of gas which lies on the other side of the plane.

The quantity of momentum thus communicated to the gas on the other side of the plane during a unit of time is a measure of the force exerted on this gas by the rest. This force is called the pressure of the gas.

If the velocities of the molecules moving in different directions were independent of one another, then the pressure at any point of the gas need not be the same in all directions, and the pressure between two portions of gas separated by a plane need not be perpendicular to that plane. Hence, to account for the observed equality of pressure in all directions, we must suppose some cause equalizing the motion in all directions. This we find in the deflection of the path of one particle by another when they come near one another. Since, however, this equalization of motion is not instantaneous, the pressures in all directions are perfectly equalized only in the case of a gas at rest, but when the gas is in a state of motion, the want of perfect equality in the pressures gives rise to the phenomena of viscosity or internal friction. The phenomena of viscosity in all bodies may be described, independently of hypothesis, as follows :—

A distortion or strain of some kind, which we may call S, is produced in the body by displacement. A state of stress or elastic force, which we may call F, is thus excited. The relation between the stress and the strain may be written $F = ES$, where E is the coefficient of elasticity for that particular kind of strain.

In a solid body free from viscosity, F will remain $=$ ES, and

$$\frac{d\mathrm{F}}{dt} = \mathrm{E}\frac{d\mathrm{S}}{dt}.$$

If, however, the body is viscous, F will not remain constant, but will tend to disappear at a rate depending on the value of F, and on the nature of the body.   If we suppose this rate proportional to F, the equation may be written

$$\frac{d\mathrm{F}}{dt} = \mathrm{E}\frac{d\mathrm{S}}{dt} - \frac{\mathrm{F}}{\mathrm{T}},$$

which will indicate the actual phenomena in an empirical manner.   For if S be constant,

$$\mathrm{F} = \mathrm{ES}e^{-\frac{t}{\mathrm{T}}},$$

showing that F gradually disappears, so that if the body is left to itself it gradually loses any internal stress, and the pressures are finally distributed as in a fluid at rest.

If $\dfrac{d\mathrm{S}}{dt}$ is constant, that is, if there is a steady motion of the body which continually increases the displacement,

$$\mathrm{F} = \mathrm{ET}\frac{d\mathrm{S}}{dt} + \mathrm{C}e^{-\frac{t}{\mathrm{T}}},$$

showing that F tends to a constant value depending on the rate of displacement.   The quantity ET, by which the rate of displacement must be multiplied to get the force, may be called the coefficient of viscosity.   It is the product of a coefficient of elasticity, E, and a time T, which may be called the "time of relaxation" of the elastic force.   In mobile fluids T is a very small fraction of a second, and E is not easily determined experimentally.   In viscous solids T may be several hours or days, and then E is easily measured.   It is possible that in some bodies T may be a function of F, and this would account for the gradual untwisting of wires after being twisted beyond the limit of perfect elasticity.   For if T diminishes as F increases, the parts of the wire furthest from the axis will yield more rapidly than the parts near the axis during the twisting process, and when the twisting force is removed, the wire will at first untwist till there is equilibrium between the stresses in the inner and outer portions.   These stresses will then undergo a gradual relaxation; but since the actual value of the stress is greater in the outer layers, it will have a more rapid rate of relaxation, so that the wire will go on gradually untwisting for some hours or days, owing to the stress on the interior portions maintaining itself

longer than that of the outer parts. This phenomenon was observed by Weber in silk fibres, by Kohlrausch in glass fibres, and by myself in steel wires.

In the case of a collection of moving molecules such as we suppose a gas to be, there is also a resistance to change of form constituting what may be called the linear elasticity, or "rigidity" of the gas, but this resistance gives way and diminishes at a rate depending on the amount of the force and on the nature of the gas.

Suppose the molecules to be confined in a rectangular vessel with perfectly elastic sides, and that they have no action on one another, so that they never strike one another, or cause each other to deviate from their rectilinear paths. Then it can easily be shown that the pressures on the sides of the vessel due to the impacts of the molecules are perfectly independent of each other, so that the mass of moving molecules will behave, not like a fluid, but like an elastic solid. Now suppose the pressures at first equal in the three directions perpendicular to the sides, and let the dimensions a, b, c of the vessel be altered by small quantities, δa, δb, δc.

Then if the original pressure in the direction of a was p, it will become

$$p\left(1 - 3\frac{\delta a}{a} - \frac{\delta b}{b} - \frac{\delta c}{c}\right);$$

or if there is no change of volume,

$$\frac{\delta p}{p} = -2\frac{\delta a}{a},$$

showing that in this case there is a "longitudinal" elasticity of form of which the coefficient is $2p$. The coefficient of "rigidity" is therefore $= p$.

This rigidity, however, cannot be directly observed, because the molecules continually deflect each other from their rectilinear courses, and so equalize the pressure in all directions. The rate at which this equalization takes place is great, but not infinite; and therefore there remains a certain inequality of pressure which constitutes the phenomenon of viscosity.

I have found by experiment that the coefficient of viscosity in a given gas is independent of the density, and proportional to the absolute temperature, so that if ET be the viscosity, $\mathrm{ET} \propto \dfrac{p}{\rho}$.

But $\mathrm{E} = p$; therefore T, the time of relaxation, varies inversely as the density and is independent of the temperature. Hence the number of collisions producing a given deflection which take place in unit of time is independent of the temperature,

that is, of the velocity of the molecules, and is proportional to the number of molecules in unit of volume.   If we suppose the molecules hard elastic bodies, the number of collisions of a given kind will be proportional to the velocity; but if we suppose them centres of force, the angle of deflection will be smaller when the velocity is greater; and if the force is inversely as the fifth power of the distance, the number of deflections of a given kind will be independent of the velocity.   Hence I have adopted this law in making my calculations.

The effect of the mutual action of the molecules is not only to equalize the pressure in all directions, but, when molecules of different kinds are present, to communicate motion from the one kind to the other.   I formerly showed that the final result in the case of hard elastic bodies is to cause the average *vis viva* of a molecule to be the same for all the different kinds of molecules.   Now the pressure due to each molecule is proportional to its *vis viva*; hence the whole pressure due to a given number of molecules in a given volume will be the same whatever the mass of the molecules, provided the molecules of different kinds are permitted freely to communicate motion to each other.

When the flow of *vis viva* from the one kind of molecules to the other is zero, the temperature is said to be the same.   Hence equal volumes of different gases at equal pressures and temperatures contain equal numbers of molecules.

This result of the dynamical theory affords the explanation of the "law of equivalent volumes" in gases.

We shall see that this result is true in the case of molecules acting as centres of force.   A law of the same general character is probably to be found connecting the temperatures of liquid and solid bodies with the energy possessed by their molecules, although our ignorance of the nature of the connexions between the molecules renders it difficult to enunciate the precise form of the law.

The molecules of a gas in this theory are those portions of it which move about as a single body.   These molecules may be mere points, or pure centres of force endowed with inertia, or the capacity of performing work while losing velocity.   They may be systems of several such centres of force bound together by their mutual actions; and in this case the different centres may either be separated, so as to form a group of points, or they may be actually coincident, so as to form one point.

Finally, if necessary, we may suppose them to be small solid bodies of a determinate form; but in this case we must assume a new set of forces binding the parts of these small bodies together, and so introduce a molecular theory of the second order. The doctrines that all matter is extended, and that no two por-

tions of matter can coincide in the same place, being deductions from our experiments with bodies sensible to us, have no application to the theory of molecules.

The actual energy of a moving body consists of two parts, one due to the motion of its centre of gravity, and the other due to the motions of its parts relative to the centre of gravity. If the body is of invariable form, the motions of its parts relative to the centre of gravity consist entirely of rotation ; but if the parts of the body are not rigidly connected, their motions may consist of oscillations of various kinds, as well as rotation of the whole body.

The mutual interference of the molecules in their courses will cause their energy of motion to be distributed in a certain ratio between that due to the motion of the centre of gravity and that due to the rotation or other internal motion. If the molecules are pure centres of force, there can be no energy of rotation, and the whole energy is reduced to that of translation ; but in all other cases the whole energy of the molecule may be represented by $\frac{1}{2}Mv^2\beta$, where β is the ratio of the total energy to the energy of translation. The ratio β will be different for every molecule, and will be different for the same molecule after every encounter with another molecule, but it will have an average value depending on the nature of the molecules, as has been shown by Clausius. The value of β can be determined if we know either of the specific heats of the gas, or the ratio between them.

The method of investigation which I shall adopt in the following paper is to determine the mean values of the following functions of the velocity of all the molecules of a given kind within an element of volume :—

(α) the mean velocity resolved parallel to each of the coordinate axes ;

(β) the mean values of functions of two dimensions of these component velocities ;

(γ) the mean values of functions of three dimensions of these velocities.

The rate of translation of the gas, whether by itself or by diffusion through another gas, is given by (α), the pressure of the gas on any plane, whether normal or tangential to the plane, is given by (β), and the rate of conduction of heat through the gas is given by (γ).

I propose to determine the variations of these quantities, due, 1st, to the encounters of the molecules with others of the same system or of a different system ; 2nd, to the action of external forces such as gravity ; and 3rd, to the passage of molecules through the boundary of the element of volume.

I shall then apply these calculations to the determination of the statical cases of the final distribution of two gases under the action of gravity, the equilibrium of temperature between two gases, and the distribution of temperature in a vertical column. These results are independent of the law of force between the molecules. I shall also consider the dynamical cases of diffusion, viscosity, and conduction of heat, which involve the law of force between the molecules.

On the Mutual Action of Two Molecules.

Let the masses of these molecules be M_1, M_2, and let their velocities resolved in three directions at right angles to each other be ξ_1, η_1, ζ_1 and ξ_2, η_2, ζ_2. The components of the velocity of the centre of gravity of the two molecules will be

$$\frac{\xi_1 M_1 + \xi_2 M_2}{M_1 + M_2}, \quad \frac{\eta_1 M_1 + \eta_2 M_2}{M_1 + M_2}, \quad \frac{\zeta_1 M_1 + \zeta_2 M_2}{M_1 + M_2}.$$

The motion of the centre of gravity will not be altered by the mutual action of the molecules, of whatever nature that action may be. We may therefore take the centre of gravity as the origin of a system of coordinates moving parallel to itself with uniform velocity, and consider the alteration of the motion of each particle with reference to this point as origin.

If we regard the molecules as simple centres of force, then each molecule will describe a plane curve about this centre of gravity, and the two curves will be similar to each other and symmetrical with respect to the line of apses. If the molecules move with sufficient velocity to carry them out of the sphere of their mutual action, their orbits will each have a pair of asymptotes inclined at an angle $\frac{\pi}{2} - \theta$ to the line of apses. The asymptotes of the orbit of M_1 will be at a distance b_1 from the centre of gravity, and those of M_2 at a distance b_2, where

$$M_1 b_1 = M_2 b_2.$$

The distance between two parallel asymptotes, one in each orbit, will be

$$b = b_1 + b_2.$$

If, while the two molecules are still beyond each other's action, we draw a straight line through M_1 in the direction of the relative velocity of M_1 to M_2, and draw from M_2 a perpendicular to this line, the length of this perpendicular will be b, and the plane including b and the direction of relative motion will be the plane of the orbits about the centre of gravity.

When, after their mutual action and deflection, the molecules have again reached a distance such that there is no sensible action between them, each will be moving with the same velocity relative to the centre of gravity that it had before the mutual action, but the direction of this relative velocity will be turned through an angle 2θ in the plane of the orbit.

The angle θ is a function of the relative velocity of the molecules and of b, the form of the function depending on the nature of the action between the molecules.

If we suppose the molecules to be bodies, or systems of bodies, capable of rotation, internal vibration, or any form of energy other than simple motion of translation, these results will be modified. The value of θ and the final velocities of the molecules will depend on the amount of internal energy in each molecule before the encounter, and on the particular form of that energy at every instant during the mutual action. We have no means of determining such intricate actions in the present state of our knowledge of molecules ; so that we must content ourselves with the assumption that the value of θ is, on an average, the same as for pure centres of force, and that the final velocities differ from the initial velocities only by quantities which may in each collision be neglected, although in a great many encounters the energy of translation and the internal energy of the molecules arrive, by repeated small exchanges, at a final ratio, which we shall suppose to be that of 1 to $\beta-1$.

We may now determine the final velocity of M_1 after it has passed beyond the sphere of mutual action between itself and M_2.

Let V be the velocity of M_1 relative to M_2, then the components of V are

$$\xi_1-\xi_2, \quad \eta_1-\eta_2, \quad \zeta_1-\zeta_2.$$

The plane of the orbit is that containing V and b. Let this plane be inclined ϕ to a plane containing V and parallel to the axis of x; then, since the direction of V is turned round an angle 2θ in the plane of the orbit, while its magnitude remains the same, we may find the value of ξ_1 after the encounter. Calling it ξ'_1,

$$\left. \begin{array}{l} \xi'_1 = \xi_1 + \dfrac{M_2}{M_1+M_2} \{(\xi_2-\xi_1)2\sin^2\theta \\[2mm] + \sqrt{(\eta_2-\eta_1)^2+(\zeta_2-\zeta_1)^2}\sin 2\theta \cos\phi\}. \end{array} \right\} \quad \cdot \quad \cdot \quad (1)$$

There will be similar expressions for the components of the final velocity of M_1 in the other coordinate directions.

If we know the initial positions and velocities of M_1 and M_2, we can determine V the velocity of M_1 relative to M_2, b the shortest distance between M_1 and M_2 if they had continued to

move with uniform velocity in straight lines, and ϕ the angle which determines the plane in which V and b lie. From V and b we can determine θ, if we know the law of force; so that the problem is solved in the case of two molecules.

When we pass from this case to that of two systems of moving molecules, we shall suppose that the time during which a molecule is beyond the action of other molecules is so great compared with the time during which it is deflected by that action, that we may neglect both the time and the distance described by the molecules during the encounter, as compared with the time and the distance described while the molecules are free from disturbing force. We may also neglect those cases in which three or more molecules are within each other's spheres of action at the same instant.

On the Mutual Action of Two Systems of Moving Molecules.

Let the number of molecules of the first kind in unit of volume be N_1, the mass of each being M_1. The velocities of these molecules will in general be different both in magnitude and direction. Let us select those molecules the components of whose velocities lie between

$$\xi_1 \text{ and } \xi_1 + d\xi_1, \quad \eta_1 \text{ and } \eta_1 + d\eta_1, \quad \zeta_1 \text{ and } \zeta_1 + d\zeta_1,$$

and let the number of these molecules be dN_1. The velocities of these molecules will be very nearly equal and parallel.

On account of the mutual actions of the molecules, the number of molecules which at a given instant have velocities within given limits will be definite, so that

$$dN_1 = f_1(\xi_1 \eta_1 \zeta) d\xi_1 d\eta_1 d\zeta_1. \quad \bullet \quad \bullet \quad \bullet \quad \bullet \quad (2)$$

We shall consider the form of this function afterwards.

Let the number of molecules of the second kind in unit of volume be N_2, and let dN_2 of these have velocities between ξ_2 and $\xi_2 + d\xi_2$, η_2 and $d\eta_2 + \eta_2$, ζ_2 and $\zeta_2 + d\zeta_2$, where

$$dN_2 = f_2(\xi_2 \eta_2 \zeta_2) d\xi_2 d\eta_2 d\zeta_2.$$

The velocity of any of the dN_1 molecules of the first system relative to the dN_2 molecules of the second system is V, and each molecule M_1 will in the time δt describe a relative path $V\delta t$ among the molecules of the second system. Conceive a space bounded by the following surfaces. Let two cylindrical surfaces have the common axis $V\delta t$ and radii b and $b + db$. Let two planes be drawn through the extremities of the line $V\delta t$ perpendicular to it. Finally, let two planes be drawn through $V\delta t$ making angles ϕ and $\phi + d\phi$ with a plane through V parallel to

the axis of x. Then the volume included between the four planes and the two cylindric surfaces will be $Vbdbd\phi\delta t$.

If this volume includes one of the molecules M_2, then during the time δt there will be an encounter between M_1 and M_2, in which b is between b and $b+db$, and ϕ between ϕ and $\phi+d\phi$.

Since there are dN_1 molecules similar to M_1 and dN_2 similar to M_2 in unit of volume, the whole number of encounters of the given kind between the two systems will be

$$Vbdbd\phi\delta td N_1 dN_2.$$

Now let Q be any property of the molecule M_1, such as its velocity in a given direction, the square or cube of that velocity or any other property of the molecule which is altered in a known manner by an encounter of the given kind, so that Q becomes Q' after the encounter, then during the time δt a certain number of the molecules of the first kind have Q changed to Q', while the remainder retain the original value of Q, so that

$$\delta QdN_1 = (Q'-Q)Vbdbd\phi\delta td N_1 dN_2,$$

or

$$\frac{\delta QdN_1}{\delta t} = (Q'-Q)Vbdbd\phi d N_1 dN_2. \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

Here $\dfrac{\delta QdN_1}{\delta t}$ refers to the alteration in the sum of the values of Q for the dN_1 molecules, due to their encounters of the given kind with the dN_2 molecules of the second sort. In order to determine the value of $\dfrac{\delta QN_1}{\delta t}$, the rate of alteration of Q among all the molecules of the first kind, we must perform the following integrations :—

1st, with respect to ϕ from $\phi=0$ to $\phi=2\pi$.

2nd, with respect to b from $b=0$ to $b=\infty$. These operations will give the results of the encounters of every kind between the dN_1 and dN_2 molecules.

3rd, with respect to dN_2, or $f_2(\xi_2\eta_2\zeta_2)d\xi_2 d\eta_2 d\zeta_2$.

4th, with respect to dN_1, or $f_1(\xi_1\eta_1\zeta_1)d\xi_1 d\eta_1 d\zeta_1$.

These operations require in general a knowledge of the forms of f_1 and f_2.

1st. *Integration with respect to ϕ.*

Since the action between the molecules is the same in whatever plane it takes place, we shall first determine the value of $\displaystyle\int_0^{2\pi}(Q'-Q)d\phi$ in several cases, making Q some function of ξ, η, and ζ.

(α) Let $Q = \xi_1$ and $Q' = \xi'_1$, then

$$\int_0^{2\pi} (\xi'_1 - \xi_1) d\phi = \frac{M_2}{M_1 + M_2} (\xi_2 - \xi_1) 4\pi \sin^2\theta. \quad . \quad (4)$$

(β) Let $Q = \xi_1^2$ and $Q' = \xi'_1{}^2$,

$$\int_0^{2\pi} (\xi'_1{}^2 - \xi_1^2) d\phi = \frac{M_2}{(M_1 + M_2)^2} \{ (\xi_2 - \xi_1)(M_1\xi_1 + M_2\xi_2) 8\pi \sin^2\theta$$
$$+ M_2 \big((\eta_2 - \eta_1)^2 + (\zeta_2 - \zeta_1)^2 - 2(\xi_2 - \xi_1)^2 \big) \pi \sin^2 2\theta \}. \quad (5)$$

By transformation of coordinates we may derive from this

$$\int_0^{2\pi} (\xi'_1 \eta'_1 - \xi_1 \eta_1) d\phi = \frac{M_2}{(M_1 + M_2)^2} \{ (M_2 \xi_2 \eta_2 - M_1 \xi_1 \eta_1$$
$$+ \tfrac{1}{2}(M_1 - M_2)(\xi_1 \eta_2 + \xi_2 \eta_1)) 8\pi \sin^2\theta - 3M_2(\xi_2 - \xi_1)(\eta_2 - \eta_1) \}, \quad (6)$$

with similar expressions for the other quadratic functions of ξ, η, ζ.

(γ) Let $Q = \xi_1(\xi_1^2 + \eta_1^2 + \zeta_1^2)$, and $Q' = \xi'_1(\xi'_1{}^2 + \eta'_1{}^2 + \zeta'_1{}^2)$; then putting

$$\xi_1^2 + \eta_1^2 + \zeta_1^2 = V_1^2, \quad \xi_1\xi_2 + \eta_1\eta_2 + \zeta_1\zeta_2 = U, \quad \xi_2^2 + \eta_2^2 + \zeta_2^2 = V_2^2,$$

and $(\xi_2 - \xi_1)^2 + (\eta_2 - \eta_1)^2 + (\zeta_2 - \zeta_1)^2 = V^2$, we find

$$\int_0^{2\pi} (\xi'_1 V'_1{}^2 - \xi_1 V_1^2) d\phi = \frac{M_2}{M_1 + M_2} 4\pi \sin^2\theta \{ (\xi_2 - \xi_1) V_1^2 + 2\xi_1(U - V_1^2) \left.\right\}$$
$$+ \left(\frac{M_2}{M_1 + M_2} \right)^2 (8\pi \sin^2\theta - 3\pi \sin^2 2\theta) 2(\xi_2 - \xi_1)(U - V_1^2)$$
$$+ \left(\frac{M_2}{M_1 + M_2} \right)^2 (8\pi \sin^2\theta + 2\pi \sin^2 2\theta) \xi_1 V^2$$
$$+ \left(\frac{M_2}{M_1 + M_2} \right)^3 (8\pi \sin^2\theta - 2\pi \sin^2 2\theta) 2(\xi_2 - \xi_1) V^2. \quad \left.\right\} \cdot (7)$$

These are the principal functions of ξ, η, ζ whose changes we shall have to consider; we shall indicate them by the symbols α, β, or γ, according as the function of the velocity is of one, two, or three dimensions.

2nd. *Integration with respect to* b.

We have next to multiply these expressions by $b\,db$, and to integrate with respect to b from $b = 0$ to $b = \infty$. We must bear in mind that θ is a function of b and V, and can only be deter-

mined when the law of force is known. In the expressions which we have to deal with, θ occurs under two forms only, namely $\sin^2 \theta$ and $\sin^2 2\theta$. If, therefore, we can find the values of

$$B = \int_0^\infty 4\pi b\,db \sin^2 \theta, \text{ and } B_2 = \int_0^\infty \pi b\,db \sin^2 2\theta, \quad . \quad (8)$$

we can integrate all the expressions with respect to b.

B_1 and B_2 will be functions of V only, the form of which we can determine only in particular cases, after we have found θ as a function of b and V.

Determination of θ for certain laws of Force.

Let us assume that the force between the molecules M_1 and M_2 is repulsive and varies inversely as the nth power of the distance between them, the value of the moving force at distance unity being K, then we find by the equation of central orbits,

$$\frac{\pi}{2} - \theta = \int_0^{x'} \frac{dx}{\sqrt{1 - x^2 - \dfrac{2}{n-1}\left(\dfrac{x}{\alpha}\right)^{n-1}}}, \quad . \quad . \quad (9)$$

where $x = \dfrac{b}{r}$, or the ratio of b to the distance of the molecules at a given time: x is therefore a numerical quantity; α is also a numerical quantity and is given by the equation

$$\alpha = b\left(\frac{V^2 M_1 M_2}{K(M_1 + M_2)}\right)^{\frac{1}{n-1}} \quad . \quad . \quad . \quad . \quad (10)$$

The limits of integration are $x = 0$ and $x = x'$, where x' is the least positive root of the equation

$$1 - x^2 - \frac{2}{n-1}\left(\frac{x}{\alpha}\right)^{n-1} = 0. \quad . \quad . \quad . \quad (11)$$

It is evident that θ is a function of α and n, and when n is known θ may be expressed as a function of α only.

Also

$$b\,db = \left(\frac{K(M_1 + M_2)}{V^2 M_1 M_2}\right)^{\frac{2}{n-1}} \alpha\,d\alpha; \quad . \quad . \quad . \quad (12)$$

so that if we put

$$A_1 = \int_0^\infty 4\pi\alpha\,d\alpha \sin^2 \theta, \quad A_2 = \int_0^\infty \pi\alpha\,d\alpha \sin^2 2\theta, \quad . \quad (13)$$

A_1 and A_2 will be definite numerical quantities which may be

ascertained when n is given, and B_1 and B_2 may be found by

multiplying A_1 and A_2 by $\left(\dfrac{K(M_1+M_2)}{M_1M_2}\right)^{\frac{2}{n-1}} V^{\frac{-4}{n-1}}$.

Before integrating further we have to multiply by V, so that the form in which V will enter into the expressions which have to be integrated with respect to dN_1 and dN_2 will be

$$V^{\frac{n-5}{n-1}}.$$

It will be shown that we have reason from experiments on the viscosity of gases to believe that $n=5$. In this case V will disappear from the expressions of the form (3), and they will be capable of immediate integration with respect to dN_1 and dN_2. If we assume $n=5$ and put $\alpha^4 = 2\cot^2 2\phi$ and $x = \sqrt{1-\tan^2\phi}\cos\psi$,

$$\left. \begin{aligned} \frac{\pi}{2}-\theta &= \sqrt{\cos 2\phi}\int_0^{\frac{\pi}{2}}\frac{d\psi}{\sqrt{1-\sin^2\phi\sin^2\psi}} \\ &= \sqrt{\cos 2\phi}\,F_{\sin\phi}, \quad\ldots\ldots \end{aligned} \right\} \quad . \quad (14)$$

where $F_{\sin\phi}$ is the complete elliptic function of the first kind and is given in Legendre's Tables. I have computed the following Table of the distance of the asymptotes, the distance of the apse, the value of θ, and of the quantities whose summation leads to A_1 and A_2.

ϕ.		b.	Distance of apse.	θ.		$\dfrac{\sin^2\theta}{\sin^2 2\phi}$.	$\dfrac{\sin^2 2\theta}{\sin^2 2\phi}$.
°	′			°	′		
0	0	infinite	infinite	0	0	0	0
5	0	2381	2391	0	31	·00270	·01079
10	0	1658	1684	1	53	·01464	0·3689
15	0	1316	1366	4	47	·02781	·11048
20	0	1092	1172	8	45	·05601	·21885
25	0	916	1036	14	15	·10325	·38799
30	0	760	931	21	42	·18228	·62942
35	0	603	845	31	59	·31772	·71433
40	0	420	772	47	20	·55749	1·02427
41	0	374	758	51	32	·62515	·96763
42	0	324	745	56	26	·70197	·85838
43	0	264	732	62	22	·78872	·67868
44	0	187	719	70	18	·88745	·40338
44	30	132	713	76	1	·94190	·21999
45	0	0	707	90	0	1·00000	·00000

$$A_1 = \int 4\pi\alpha\, d\alpha\,\sin^2\theta = 2\cdot6595, \quad . \quad . \quad . \quad (15)$$

$$A_2 = \int \pi\alpha\, d\alpha\,\sin^2 2\theta = 1\cdot3682. \quad . \quad . \quad . \quad (16)$$

The paths described by molecules about a centre of force S, repelling inversely as the fifth power of the distance, are given in the figure.

The molecules are supposed to be originally moving with equal velocities in parallel paths, and the way in which their deflections depend on the distance of the path from S is shown by the different curves in the figure.

✻ S
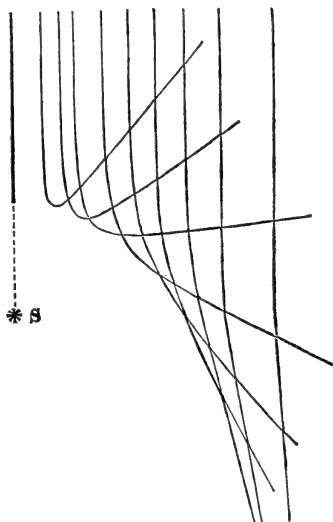
3rd. *Integration with respect to $d\mathrm{N}_1$.*

We have now to integrate expressions involving various functions of ξ, η, ζ, and V with respect to all the molecules of the second sort. We may write the expression to be integrated

$$\iiint \mathrm{Q} \mathrm{V}^{\frac{n-5}{n-1}} f_2(\xi_2 \eta_2 \zeta_2) d\xi_2 d\eta_2 d\zeta_2,$$

where Q is some function of ξ, η, ζ, &c., already determined, and f_2 is the function which indicates the distribution of velocity among the molecules of the second kind.

In the case in which $n = 5$, V disappears, and we may write the result of integration

$$\overline{\mathrm{Q}} \mathrm{N}_2,$$

where $\overline{\mathrm{Q}}$ is the mean value of Q for all the molecules of the second kind, and N_2 is the number of those molecules.

If, however, n is not equal to 5, so that V does not disappear, we should require to know the form of the function f_2 before we could proceed further with the integration.

The only case in which I have determined the form of this function is that of one or more kinds of molecules which have by their continual encounters brought about a distribution of velocity such that the number of molecules whose velocity lies within given limits remains constant. In the Philosophical Magazine for January 1860, I have given an investigation of this case, founded on the assumption that the probability of a molecule having a velocity resolved parallel to x lying between given limits is not in any way affected by the knowledge that the molecule has a given velocity resolved parallel to y. As this assumption may appear precarious, I shall now determine the form of the function in a different manner.

[To be continued.]

XVI. *On Silvering Glass.* By JUSTUS VON LIEBIG[*].

THE following are the proportions which a long series of experiments has led me to adopt as the best for preparing silver looking-glasses.

Solution of Silver.—One part of fused nitrate of silver is dissolved in ten parts of distilled water.

Solution of Ammonia.—(a) Commercial nitric acid free from chlorine is neutralized with sesquicarbonate of ammonia and the solution diluted to the specific gravity 1·115. For 37 parts of nitric acid of 1·29, 14 parts of sesquicarbonate are wanted; yet, as the sesquicarbonate does not always contain the same amount of ammonia, the proportion is not quite definite.

Nitrate of ammonia may be advantageously replaced by sulphate of ammonia.

(b) 242 grammes of sulphate of ammonia are dissolved in water, and the volume made up to 1200 cubic centims.; the specific gravity of this solution is 1·105 to 1·106.

Caustic Soda.—This must be prepared from carbonate of soda free from chlorine, and have a specific gravity of 1·05; 3 volumes of a lye of 1·035 specific gravity, such as is obtained in the manufacture, when evaporated to 2 volumes yield a lye of 1·05.

A. *Silvering-Mixture.*

100 volumes of solution of ammonia.
140 „   „ silver.
750 „ soda-lye.
―――
990

If sulphate of ammonia be used, the solution of sulphate of ammonia must be poured into the solution of silver, and then the soda-lye added in small portions; after mixing, the liquor is turbid, and must stand at least three days before being used. The clear solution is drawn off with a siphon.

Reducing-Liquid.—(a) 50 grammes of white sugarcandy are dissolved in water to a thin syrup, 3·1 grms. of tartaric acid are then added and kept boiling for an hour; the liquid is then diluted with water to the volume of 500 cubic centims.

(b) Water is poured on 2·857 grammes of tartrate of copper, and soda-lye added by drops until the blue powder is dissolved. The solution is diluted to the volume of 500 cubic centims.

B. *Reducing-Mixture.*—1 volume of the solution of sugar (a) is mixed with 1 of the solution of copper (b), and 8 volumes of water added, so as to make the whole 10 volumes.

C. *Silvering-Liquid.*

50 volumes of the silvering-mixture (A).
10 „ „ reducing „ (B).
250 to 300 „ of water.

―――――

[*] Translated from Liebig's *Annalen* (Supplement), vol. v. p. 259.

In silvering, the plates are placed in pairs vertically in the trough, the silvering-solution A is mixed with water in a separate vessel, the reducing-liquid mixed, and the trough filled; in winter it is convenient to use warm water, so that the temperature may be from 20° to 28°.

Glasses for optical purposes must be silvered in a horizontal position, so as to touch the surface of the liquid; the silver surface must be transparent with a blue colour; it must be brilliant, and must adhere so firmly that it is not rubbed off when polished.

This mode of silvering is calculated for the manufacture of mirrors the cost of preparing which shall not exceed that of the commonest sorts. Special determinations show that' with these mixtures perfect mirrors can be prepared with a quantity of silver not exceeding 3 to $3\frac{1}{2}$ grammes in a square metre.

Without the addition of copper this cannot be effected ; I am not in a position to give an explanation of this. The action of copper is at once recognized, if a very dilute solution free from copper be mixed with solution of sugar and allowed to stand; the deposit of silver is then full of white spots and of holes; if a trace of copper be present, the deposit is lustrous and free from faults ; and with more copper no silver is deposited. In this case there are actions of adhesion at work quite out of the range of theoretical considerations. The point is to give the particles of the liquid less adhesion to the silver than is possessed by the particles of the glass whose surface is moistened by the liquid; when the adhesion of the particles is greater, the glass is not coated.

The silvering in a large looking-glass manufactory near Nuremberg has been effected by the above process for more than a year, and produced very beautiful articles, which, however, met with no sale. It is to be expected that in the course of time the prejudices against silver looking-glasses will disappear.

XVII. *Proceedings of Learned Societies.*

ROYAL SOCIETY.

[Continued from vol. xxxiv. p. 545.]

Dec. 5, 1867.—Dr. W. A. Miller, Treas. and V.P., in the Chair.

THE following communication was read :—

"On some Alterations in the Composition of Carbonate-of-Lime Waters, depending on the influence of Vegetation, Animal Life, and Season." By ROBERT WARINGTON, F.R.S., F.C.S.

In carrying out through a series of years the principles of the aquarium for sustaining animal life in a confined and limited portion of water through the medium of growing vegetation *, I had observed that, during the summer months of the year, a consider-

able deposit made its appearance on the leaves of the plants and the glass front of the containing vessel, which was found to consist of carbonate of lime in a crystalline condition. This deposit formed a nidus for the growth of confervoid vegetation, which, at certain seasons of the year, increased very rapidly. These observations were alluded to at one of the Friday-evening meetings of the Royal Institution, March 27, 1857, when portions of the deposit were exhibited, and its composition demonstrated by experiment.

The formation of this deposit was then explained as arising from the fact that, as the summer season advances, and we have a longer continuance and also a greater intensity of the light of the sun, the absorption and consequent decomposition of carbonic acid by the plants is carried to a much greater extent, while the quantity of carbonic acid produced by the fish remains unchanged. The solvent of the carbonate of lime contained in the water being thus withdrawn, a deposit slowly takes place, incrusting the sides of the tank, particularly towards the light, where the confervoid growth, consequent upon it, accumulates in large quantities.

In continuing these observations, my attention was particularly arrested by the steady increase of deposition, attendant upon the renewed activity of the leaves, during the spring; and this determined me to ascertain by experiment the quantity of carbonate of lime existent in the water at fixed intervals during a long period of time. And inasmuch as the degrees of hardness, indicated by the measures of Clark's soap-test, presented a very ready, accurate, and simple means of arriving at this result, that mode of estimation was adopted, care being taken to displace any uncombined carbonic acid by agitating the sample with atmospheric air prior to the addition of the test, as directed by Dr. Clark, the indications or degrees thus obtained representing the quantity of lime-salts contained in an imperial gallon of the sample (70·000 grains of distilled water) in terms of carbonate of lime.

In order that the nature of the experiment may be more clearly understood, it will perhaps be better for me, before stating the results thus obtained, to describe briefly the construction and arrangement of the aquarium, its position, and its contents. The tank consisted of a rectangular zinc framing, twenty inches long by thirteen broad, and twenty-one in depth, having slate cemented into it at the bottom and sides, and being glazed at the back and front. It was filled with water to the height of twelve inches, or a volume equal to ten gallons, and on the slate sides were cemented, at the water-line, ledges of rockwork composed of sandstone and tufaceous limestone from Matlock, on which were planted a few ferns, chiefly Trichomanes, for ornament. The bottom of the tank was covered, for about two inches, with a mixture of sandy loam and gravel, into which several plants of the *Vallisneria spiralis*, the vegetable member of the arrangement, were inserted. Some large fragments of rough rockwork, principally limestone, were also placed upright on the bottom to break up the stiff outline of the square framing, and give a pleasing effect to the eye. The animal branch of the circle

consisted of four small crucian carp with a gold carp.   Several freshwater mollusks, principally *Planorbis corneus* and *Limneus palustris,* were also introduced to act as scavengers and consume the decaying vegetation.   The tank was loosely covered with a plate of glass, so as to allow of a free admission of the external air, and at the same time keep out a great deal of the soot and dust of the London atmosphere and impede the too rapid evaporation of the water.   As the Trichomanes were stated to delight in shade, a thin muslin blind was placed over the covering glass.

The aquarium was located in a window-way having an eastern aspect, but, being surrounded within a few yards by the high walls of adjoining houses, the direct rays of the sun only reached it for about three hours in the morning during the months of June and July.   It was established in January 1851, and has not since been disturbed, except by occasional supplies of distilled or rain-water, to replace the loss in volume arising from evaporation.   It had been my custom to weed out the excessive growth of the Vallisneria during the summer, and also to remove some of the flaky deposit of calcareous matter from the surface of the glass nearest the light; but as I considered that such disturbances might interfere with the course of the investigation, these operations were discontinued.

The results that have been obtained from this investigation during the years 1861 and 1862 are as follows :—

1861.	March 13	....	26·2	⎧ degrees of hardness, or grains of lime-	
				⎨ salts, per imperial gallon, in terms	
				⎩ of carbonate of lime.	
	May	1	19·5	,,	,,
	July	3	12·5	,,	,,
	August	1	13·6	,,	,,
	Sept.	17	15·0	,,	,,
	Oct.	8	15·5	,,	,,
	Nov.	12	18·0	,,	,,
	Dec.	9	20·5	,,	,,
1862.	Jan.	8	23·5	,,	,,
	Feb.	8	25·0	,,	,,
	March	3	23·0	,,	,,
	April	3	21·0	,,	,,
	May	2	19·0	,,	,,
	June	4	16·5	,,	,,
	July	4	14·0	,,	,,
	August	5	12·0	,,	,,
	Sept.	2	12·5	,,	,,

The amount of calcareous matter dissolved will be seen to have steadily decreased during the spring and summer months, from its maximum in March 1861 and February 1862 to its minimum in July 1861 and August 1862, and then to have increased as steadily during the autumn and winter months.

Part of this hardness, however, unquestionably arose from the presence in the water of other salts of lime besides the carbonate.

To determine how much was the next point for investigation. Portions of the water were taken on several occasions and boiled for a considerable time, filtered, and the volume restored to its original bulk with distilled water. On examining these portions with the soap-test, it was found that the hardness was lowered to 5·6 degrees, equivalent to 5·6 grains of carbonate of lime. But inasmuch as carbonate of lime is soluble in water to the extent of 2·4 grains in the imperial gallon*, this will be reduced to 3·2 grains, which amount will therefore have to be deducted from each of the above results, in order to arrive at the true quantity of carbonate present in solution.

The maximum and minimum results will then stand thus :—

	CaO, CO_2 in the imperial gallon.		CaO, CO_2 in the imperial gallon.
1861. { Maximum....	23·0	1862. { Maximum	21·8
Minimum	9·3	Minimum	8·8

The data thus obtained will help to elucidate several very important and interesting phenomena in respect to all the three elements of the arrangement—the water, the fish, and the vegetation.

1. *The Water.*

The importance of growing submerged vegetation in maintaining waters, rich in carbonate of lime, in a meliorated state by diminishing their hardness has been clearly demonstrated by the foregoing data; and how necessary, therefore, it is that this association should be kept in view whenever a soft and healthful water is required for domestic purposes. Unfortunately this appears hitherto not to have been well understood, or at all events has been little attended to, since the very agent which has been provided naturally for effecting these beneficial results has been most commonly regarded as an evil, and studiously eradicated in all directions. These data will also explain the cause of the rapid growth of vegetation in well-waters rich in carbonic acid, when pumped into tanks or reservoirs and exposed to the full light of day. The plant-germs, naturally contained in the water or absorbed from the atmosphere, being supplied with an abundance of appropriate nourishment, rapidly vegetate, and the containing vessels, particularly during the summer months, soon become thickly coated with a dense confervoid growth.

It will also follow that all fish, as generators of carbonic acid, should be excluded from waters flowing over carbonate-of-lime strata, and intended for the supply of towns &c., as tending to increase their hardness. Of course the absence of calcareous matter would prevent such an effect taking place—a fact borne out by the well-known softness of springs and rivers flowing out of or over granite or sandstone rocks, even when thickly inhabited by the scaly tribe.

* Chemical Report on the Supply of Water to the Metropolis, June 17, 1851, by Messrs. Graham, Miller, and Hofmann; and Quarterly Journal of the Chemical Society, vol. iv. p. 381.

2. *The Fish.*

It is well known that water has the property of absorbing air from the surrounding atmosphere, and holding it in solution to the extent of from one-fortieth to one-thirtieth of its volume, not, however, without somewhat changing the proportion of its constituents; for when the absorbed air is abstracted from water it usually contains about thirty-two per cent. of oxygen gas, instead of twenty-one. This oxygen is converted by the respiration of the fish into carbonic acid, which is held dissolved by a still stronger affinity, the water being capable of retaining as much as its own volume of this gas in solution at the ordinary temperature and pressure of the atmosphere.

In the above-described arrangement the carbonic acid thus produced is absorbed by the submerged vegetation under the influence of the sun's light; the carbon is appropriated for its growth, while the oxygen is again liberated and held in solution by the water, provided the evolution is not too rapid, an effect produced by too great an exposure to the sun's light. When this is the case, much of the oxygen necessarily escapes into the air in a gaseous state and is lost. During the winter season, however, when the active functions of vegetation are to a great extent dormant, from the diminished quantity and intensity of the sun's light, the amount of carbonic acid produced by the respiration of the fish is greater than the plants are capable of consuming, and the excess must necessarily accumulate in the water. Were the production of carbonic acid confined to a short period, the water would doubtless right itself after a time, the poisonous gas passing away and fresh atmospheric air being absorbed. As, however, the production of carbonic acid is constant, this ameliorating action can have little effect; the water must remain always highly charged with carbonic acid. Here, then, its solvent action on the carbonate of lime, present in the rockwork and gravel, comes into play, and the hardness of the water is gradually increased in proportion as the light diminishes. Now, supposing for an instant that no carbonate of lime had been present in the arrangement, the question arises, what must then have ensued? The fish would have continued to respire, and would produce carbonic acid as before, which, remaining in a free state dissolved in the water, would unquestionably have had a most detrimental effect upon their health. Every one must have noticed the manner in which the golden carp confined in a globe of water, in which there is no growing vegetation to decompose the carbonic acid generated, or no limestone to combine with it, rise to the surface and continually gulp in the air required for their vital functions. Nothing whatever of this kind has ever been noticed in the aquarium under consideration, although the quantity of carbonic acid dissolved in the water has been at times very large.

From the experiments of Bischof[*], we glean that the carbonic

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[*] Bischof's 'Elements of Chemical Geology,' Cavendish Society's edition, vol. iii. p. 5.

acid contained in a saturated aqueous solution is entirely displaced by a current of atmospheric air passed through it for five minutes; and also [*] that, by the same means, a solution of carbonate of lime, in water previously saturated with carbonic acid, will have all the excess of gas displaced in fifteen minutes, leaving the water with *bicarbonate of lime* in solution. It is in this form of combination that MM. Peligot [†] and Poggiale [‡] consider the carbonate of lime to exist in the water of the Seine, and M. Bineau [§] in that of the Rhone, in which rivers they state there is no free carbonic acid. In the present investigation we shall therefore assume it to be in the same state of combination. We have, in the series of experiments detailed above, an increase in the quantity of carbonate of lime held in solution, amounting to 14·2 grains in the imperial gallon, which would require nearly $6\frac{1}{4}$ grains of carbonic-acid gas to dissolve it. Besides this there is also the quantity already present in the water at its minimum, which amounts to nearly four grains more, or in all to about ten grains, equal to nearly 215 cubic inches of that gas in the ten gallons of water, or more than $\frac{1}{13}$th its volume. The exact numbers will be seen in the following Table:—

CaO, CO_2 in the gallon. CO_2.

$$1861 \begin{cases} \text{Maximum } 23\cdot0 \text{ grs., requiring } 10\cdot120 \text{ grs. to form } CaO,2CO_2. \\ \text{Minimum } \quad 9\cdot3 \quad ,, \qquad ,, \qquad 4\cdot092 \quad ,, \qquad ,, \qquad ,, \end{cases}$$

$$1862 \begin{cases} \text{Maximum } 21\cdot8 \quad ,, \qquad ,, \qquad 9\cdot592 \quad ,, \qquad ,, \qquad ,, \\ \text{Minimum } \quad 8\cdot8 \quad ,, \qquad ,, \qquad 3\cdot872 \quad ,, \qquad ,, \qquad ,, \end{cases}$$

Car. acid required to dissolve the increase 6·248 grs. = 13·269 cub. in.

,,   ,,   minimum 3·872 ,,   8·228 ,,

           10·120 ,,   21·497 ,,

Yet, although the quantity of poisonous gas had been thus increased, we find no deleterious action on the health of the fish, no disturbance in the ordinary respiration, no gulping at the surface of the water for fresh air. It is quite evident, therefore, that the carbonic acid, by entering into combination with carbonate of lime, however weak that combination may be, is thereby rendered perfectly innocuous, and a wonderful provision is thus afforded for preventing this poisonous agent from becoming fatal to animal life.

We turn now to the next member of our arrangement.

3. *The Vegetation.*

It will be seen from the foregoing numerical results that the maximum quantity of dissolved carbonate of lime, and consequently of carbonic acid, is found just before the period of the reviving energies of the plant's growth, namely, the spring time of the year, when the days are lengthening and the sun's light is continually increasing in strength; the minimum quantity when this growth

[*] *Op. cit.* vol. iii. p. 7.
[†] Comptes Rendus, vol. xl. p. 1121, and Bischof's 'Elements,' vol. iii. p. 117.
[‡] Journal de Pharmacie, vol. xxviii. p. 321, and *cp. cit.* vol. iii. p. 118.
[§] Comptes Rendus, vol. xli. p. 511, and *op. cit.* vol. iii. p. 118.

has attained its greatest exuberance, namely, when the summer months are past and the light is beginning to decrease in its intensity and the days to shorten. So exactly, indeed, are the energies of the plants regulated by the amount of light to which they are exposed, that a constant arrangement, such as that here described, affords an excellent indication of the variation of the seasons in different years, or might even be made a rough measure of the total amount of light from month to month.

But while the demand for carbonic acid on the part of the plant varies in this manner with the seasons, the amount of that gas produced by the respiration of the fish is very nearly the same all through the year. Whence, then, does the plant obtain that additional quantity of food which its stimulated energies require during the spring and early summer months, and which its rapid and luxurious growth show to be readily supplied? After what has been stated, I think the source must be apparent to every one : it is the carbonic acid which has been gradually accumulated, and rendered innocuous to animal life from its being held in combination with carbonate of lime, in so marvellous a manner during the winter months. Stored up, yet held in feeble combination, a combination so weak that the vital forces of the fresh-growing vegetation can easily overcome it, and resolve once more into carbonate of lime, carbon, and oxygen the bicarbonate of lime contained in the water *.

Thus beautifully are the necessary irregularities in the purifying action of the plant compensated and provided for, that the balance of existence between the animal and vegetable organisms be not disturbed or overthrown, and thus additional proof is furnished, if such were needed, of the wisdom of that creative power that has ordered all things to work together for good, and by endowing certain bodies with such seemingly minute and insignificant affinities, maintains the glorious harmony of the whole.

GEOLOGICAL SOCIETY.

[Continued from vol. xxxiv. p. 549.]

January 8, 1868.—Warington W. Smyth, M.A., F.R.S., President, in the Chair.

The following communications were read :—

1. " Notes on the Lower Lias of Bristol." By W. W. Stoddart, Esq., F.G.S.

Three sections in the suburbs of Bristol were described by the author as exhibiting the following strata in descending order, namely:—at Ashley Down, (1) *Ammonites-costatus* bed, (2) Saurian bed, (3) *Ammonites-Conybeari* bed (commencement of the zone of *A. Bucklandi*), and (4) Lima-beds; the succeeding beds are covered up for a short distance, and then, in Montpelier quarry, are exposed (5) *Ammonites-torus* bed, (6) Echinoderm-beds, (7) *Ammonites-*

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* The rapid growth of submerged vegetation in rivers and waters containing a considerable amount of carbonate of lime must have been observed by all interested in the subject, in some cases obliging the cleansing of such streams three or four times during the year.

Johnstoni beds, and (8) Avicula-bed; in Cotham quarry are seen (9) Rubble-bed containing *Ammonites planorbis, Lima gigantea,* and *L. Dunravenensis*; (10) *Ammonites-tortilis* bed, (11) Sutton-beds, (12) Pholidophorus-bed, (13) *Ammonites-Johnstoni* beds, (14) White Lias, and (15) Cotham marble resting upon the Keuper marls, the *Avicula-contorta* beds being absent. Mr. Stoddart considered that the Cotham section afforded very decided evidence of the Bridgend series being above the Rhætic beds, and in the Planorbis-zone. He also described a horizontal section of the deposits between Ashley Down and Cotham, and remarked on the physical conditions which had combined to produce the phenomena observed in the district.

2. " On the Lower Lias beds occurring at Cotham, Bedminster, and Keynsham, near Bristol." By C. O. Groom-Napier, Esq., F.G.S.

The author described in detail sections exposed in two quarries at Cotham, and noticed others seen at Bedminster and Keynsham, He had made an extensive collection of fossils from the several beds, and he now exhibited a table showing the names and ranges of the several species. The conclusions at which he had arrived were :— that the Sutton-stone is a Liassic rather than a Rhætic bed, and belongs to the Planorbis-zone; and that the Planorbis-zone and the Sutton series are subdivisions of the White Lias. Mr. Groom-Napier also described two new species from the Planorbis-zone of Cotham (namely, *Avicula Sandersi* and *Anatina Cothamiensis*), and one (*Hinnites minutus*) found in a stratum at Cotham associated with *Monotis decussata.*

3. " On the Dentition of *Rhinoceros Etruscus,*" Falc. By W. Boyd Dawkins, Esq., M.A., F.R.S.

The number of teeth possessed by *R. Etruscus* is the same as that of the three species already described by the author.

The first premolar, if present at all, disappeared very early in life, leaving no trace of its existence. This character separates it from all other known Miocene species. Of the milk-molars the author has not yet sufficient material to attempt a description.

The upper true molars differ from those of other British species in the lowness of their crowns, the abruptly tapering form of the colles, and the stoutness of the guard on the anterior aspect. The grinding-surface of the crown is deeply excavated, not worn flat as in *R. tichorhinus.* The horizontality of the guard, and the height above the cingulum, characterize the whole of the premolars, and distinguish this species from all others found in Britain.

The lower true molars differ from those of *R. megarhinus* in being smaller, having the crowns lower, and the guard more strongly marked. They differ from those of *R. leptorhinus* and *tichorhinus* in the position of the guard, the lowness of the crown, the thickness of the enamel, and the absence of costæ from the rounded anterior area.

R. Etruscus, together with all Miocene species (except those of the Sivalik Hills), belong to the brachydont section, while all the

living and Pliocene and Pleistocene species (except *Etruscus*) belong
to the hypodont section. We have therefore to compare *R.
Etruscus* with Miocene rather than with Pliocene and Pleistocene spe-
cies. It differs from the Rhinoceros of Auvergne principally in the
greater complexity of its *anterior valley* and the larger development
of the *posterior combing-plate.* Its nearest ally is the hornless Rhi-
noceros of Darmstadt, the *Acerotherium incisivum* of Kaup.

   R. Etruscus has been found associated with *R. megarhinus,* but not
with *R. tichorhinus* nor *R. leptorhinus.*

   It has not been found with any animal (except the Mammoth)
fitted for living in a severe climate, nor in any deposit of postglacial
age.

XVIII. *Intelligence and Miscellaneous Articles.*

ON STELLAR SPECTRA.   BY FATHER SECCHI.

I N my memoir on stellar spectra, published in the *Memorie della
  Società Italiana,* I have observed that the three principal lines of
hydrogen coincide with the dark lines of the white stars of the first
type, like α Lyræ, Sirius, &c.

   Yet the identity of these lines was only certain in the case of the
greenish blue (the line F), and very probably in that of the violet.
That of the red (H α) could not be confirmed, owing to the small
intensity of the light at this end of the spectrum. This was a defect
which needed to be remedied.

   On my return to Rome I endeavoured to improve the simplified
form of the direct-vision spectroscope; and having observed that the
ordinary eyepieces, owing to their magnifying in all directions of the
field, diminish too much the intensity in the red, I tried a cylindrical
eyepiece. It consists of an achromatic cylindrical lens with a focal
length of about 7 centims., which I substituted for the ordinary eye-
piece in my simplified spectroscope.

   The result was most surprising. This lens retains a remarkable
power even at the extremities of the spectrum; and I could immedi-
ately observe the dark line of the red Hα in its place in the stars
α Lyræ, α Pegasi, Algol, and in several other stars of the first
magnitude.

   By way of confirmation, I was desirous of seeing γ Cassiopeæ, in
which the bright lines occupy the place of the dark ones, as I have
formerly shown. In fact I could see the bright-red ray stand out
on the very feebly luminous ground. It is curious that with this
eyepiece the bright line f is less distinctly seen; but that is expli-
cable from the great light of the whole of the greenish-blue space on
which this ray is projected, and which, being greatly strengthened,
prevents the ray from standing out. The observation of Mr. Hug-
gins on this ray is thus confirmed, he having in turn confirmed my
discovery of the bright line F in the spectrum of this curious star.

   If the fine weather continues I hope I may be able to extend these
observations. I may add that o of the Whale, which is now of
almost the third magnitude, exhibits a magnificent spectrum of the
third type, resembling in beauty that of β Pegasi and α Orionis, and

as easy to resolve. This spectrum having the appearance of a colonnade, I may add that, starting from the small column near D in the yellow, three magnificent columns are found on the side towards the red, and five on the side towards the violet, all of them resolvable into finer lines—in all at least nine columns. It is one of the most curious spectra which the observation of the heavens presents. I may add that the variable stars (except Algol) belong to this type.— *Comptes Rendus*, December 9, 1867.

ON AN IMPROVED METHOD OF DIVIDING ALCOHOL AND OTHER THERMOMETERS. BY WILLIAM ACKLAND, ESQ.

In the manufacture of thermometers for low temperatures, considerable difficulties are experienced owing to equal increments of temperature not causing an equal increase of volume of the fluid employed; and this unequal expansion gives rise to considerable errors even within limited ranges of temperature.

If, in constructing an alcohol thermometer, we select a tube with uniform bore, we find, on giving it certain fixed points, corresponding to an equal number of degrees between each point, that the spaces so obtained are each diminishing in length as we descend; hence the ordinary mode of equal divisions between the ascertained points is found to give inaccurate results. An important question therefore arises,—Can we so subdivide our tube that each subdivision shall be in its proper place?

During the autumn of last year, Mr. Glaisher mentioned this subject to me, and at the same time offered some valuable suggestions to remove this difficulty, and caused me to direct my attention to this subject. Many subsequent interviews with that gentleman, extending over some months, enabled me to mature my first idea, and aided by his valuable assistance and counsel, the success aimed at has been attained; and I am now in a position to state that I have completed a dividing-engine on an entirely new principle, which may strictly be termed "Interpolating;" for, whilst between any consecutive terms taken at regular and fixed intervals we can by numerical interpolation find intermediate terms conformable to the law of the series; so, between fixed and determined points of our thermometer, we can, by using the "interpolating-engine," so divide the intervening spaces that they shall conform to the varying nature of the series, or, in other words, that the divisions shall increase in magnitude as we ascend the scale in such proportions as are demanded by the expansion of the alcohol and the bore of the tube employed.

To illustrate this new method I have invented, let us suppose we have ascertained the fixed points, P, Q, R, S, of a thermometer corresponding to equal differences of temperature. And let

$$P\,Q = x_1, \quad Q\,R = x_2, \quad R\,S = x_3$$
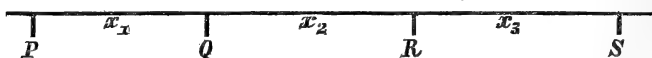
It is desired to divide the intervening spaces each into ten divisions, so that each division shall occupy its true position.

. To do this, take any right-angled triangle, A B C, and divide the side A C into ten equal parts by straight lines drawn from B.
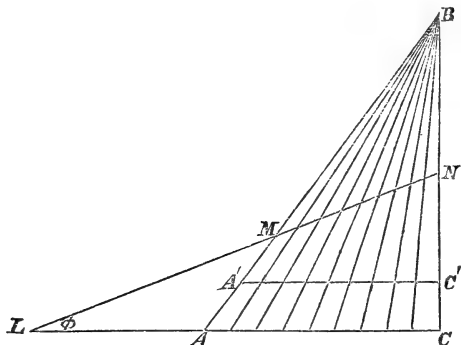
Then, if a straight line, as A' C', be drawn parallel to A C, it will be divided into ten equal parts; but if it be drawn not parallel to A C, it will be divided into ten unequal parts.

To apply this to the thermometer to be divided, draw a transversal L M N cutting A C produced in L, at an angle ϕ, so that

$$\tan \phi = \frac{x_2 - x_1}{x_2 + x_1} \tan A,$$

and

$$M N = x_1.$$

On doing this, it becomes evident that such a line, so placed, will be divided into ten unequal parts, proportionate to the law governing the series, and we can in the same manner, by using the same formula, divide any number of spaces with equal accuracy.

It remains, therefore, mechanically to transfer such divisions to our thermometer, previously marked off at equal intervals of temperature, in order to secure its correctness to even second differences.

This mechanical copying can be done by the dividing-engine before referred to; and it is worthy of note, that the formula and engine equally apply to the more correct dividing of mercurial thermometers having unequal or varying diameters of bore, as also to the construction of hydrometers of absolute accuracy.

I can easily understand that whilst the mathematician may appreciate the formula thus introduced, and also its successful application, those accustomed to the construction of thermometers would hesitate to adopt it, from the fact that the plan involves a series of calculations for each thermometer, which would involve considerable loss of time and risks of inaccuracies, if these computations were hastily done; hence my first idea was to compute a series of tables; but this was attended with only partial success. My attention was then directed to the mechanical solution of these problems, the result of which was the invention of a little

piece of apparatus, which may be called a computer, consisting of a sliding-rule, index-arm, and scale. Suppose we wish to divide accurately the space x_1, formerly given ; we set the distance from P to Q on the slide, to that of Q to R on the fixed scale, and the index-arm at once points to the angle on the scale which M N must make with A C on our divided triangle.

In use, this computer is found both trustworthy and simple, and facilitates what would otherwise have been tedious to perform and liable to inaccuracies when done.

Having devised a method of dividing a thermometer-tube accurately, I next turned my attention to the most suitable strength of alcohol to be employed in filling these thermometers; and as but little can be gained by referring to our scientific writers on this subject, I undertook a series of experiments to satisfy myself on this point.

Now it is well known that the expansion of alcohol by heat is not proportionate to its change of temperature ; and we are consequently unable to express its corresponding coefficient by a simple formula, as for metals and mercury, but must adopt the more complex expression of M. Biot,
$$d = at + bt^2,$$
where a and b are the required coefficients, and t the temperature. The coefficients of absolute alcohol are constant for all temperatures, but inasmuch as this fluid becomes weaker from momentary exposure to the air, and the mere pouring from one bottle to another not only alters its specific gravity but also its rate of expansion and its coefficient, it becomes an important point to select some other strength less liable to those changes, which only tend to inaccuracies, however much we may strive to prevent them. In making this selection, various specific gravities and of varying purities were tested, and the results led to the selection of alcohol having a specific gravity of ·815, as spirit of this strength, if pure, and *free from methylated spirit*, fusel-oil &c., has its coefficients as constant as those of absolute alcohol, and it is but little liable to undergo those changes that seem to thwart our efforts when using a stronger sample.—*From the Proceedings of the Meteorological Society for November* 20, 1867.

DIALYSIS OF INDUCED CURRENTS.
NOTE BY M. E. BOUCHOTTE.

The machine for induction-currents which was used in the following experiments is from the works of the *Alliance* Company. It has eight bobbins, each with a coil of 160 metres of copper wire 1 millim. in diameter. Eight horseshoe magnets act upon the bobbins, and at each turn of the axis produce eight positive and as many negative currents. It is worked day and night by an hydraulic wheel; it can be moved at rates between 250 and 800 turns in a minute; it has hitherto been kept at a velocity of 500 turns.

We first endeavoured to determine the electromotive force of the apparatus. For this purpose it was provided with a commutator which turned all the currents in the same direction. The circuit

included a battery of thirty-six sulphate-of-copper elements, the work of which could either be added to or subtracted from that of the induction-machine.

If F be the electromotive force of Nollet's apparatus, and f that of the battery, by means of a sine-compass, measuring the intensity of the current in the two cases, we get an approximate value for f. We have found thus $F=4f$; that is, that the induction-machine, working with its currents all in one direction, has an electromotive force equal to 144 sulphate-of-copper elements.

When the apparatus works without the commutator, the currents, acting in groups often in opposite directions, cannot produce a permanent deflection of the needle unless it be very sensitive. If a voltameter be interposed in the circuit, each electrode yields a mixture of hydrogen and oxygen gases.

In a sulphate-of-copper voltameter electrolysis is also impossible. But it will at once be seen that if by a special arrangement of the voltaic circuit, and without apparently breaking it, one of the series be absorbed, the effects of the other will appear with as much sharpness as if the electricity of a battery, or that of an induction-machine with adjusted currents, had been used.

This remarkable result may be obtained by different means,—among others, if a voltameter with acidulated water be interposed in the circuit, the electrodes of which consist of sufficiently fine platinum. These electrodes are attached to supports, by which they can be more or less immersed in the liquid. One of the wires being immersed in the voltameter, if the other be placed in contact with the surface, its point becomes incandescent. If the electrode be then allowed to sink about 7 or 8 millims. in the acidulated water, it becomes surrounded with a luminous sheath. From this moment we have a current, or rather a series of perfectly polarized currents. The direction of the deflection is such as to show that the electrode with a luminous sheath is positively charged. Interposing in the circuit another voltameter with sulphate of copper, it is seen that the plate which is in metallic contact with the luminous electrode dissolves, while metallic copper is deposited on the other.

This series of currents, freed from those of the opposite kind, traverse as many as thirty-six sulphate-of-copper elements which are arranged in opposition.

The experiment which has been cited succeeds with either of the electrodes, showing that we can at will modify the effects of each series of currents.

If the wire be more deeply immersed in the voltameter, the luminous sheath disappears, and the series of currents which was absorbed ceases to be so.—*Comptes Rendus,* November 4, 1867.

METHOD OF GALVANICALLY PRODUCING HOLLOWS AND RELIEF WITHOUT THE AID OF VARNISH. BY M. BALSAMO.

It is generally known that, in vibrating plates, points can be produced where the disturbance is almost null, and others where it is very great,—that is to say, nodal lines and segments. This is effected by

pressing the finger against any portion of the plate put in vibration by a bow. As the mechanical pressure on the vibrating plates produces symmetrically nodal lines corresponding to the point of pressure, I thought that metal plates immersed in voltaic baths might have a certain inertia at the points at which they were pressed. Facts have answered my anticipations ; metallic plates struck by electricity, though apparently motionless, emit notes which we do not hear, but which may produce designs on the surface under given conditions.

The following is the manner in which I have made the experiment. In a solution of acetate of iron to which a few grammes of phosphoric acid and some fragments of phosphorus were added, I immersed two plates of ordinary iron—one in connexion with the positive, and the other with the negative pole of a Bunsen's battery of three elements. Between these two plates and at right angles to their surface I fixed a glass plate 210 millims. in length and 35 millims. square, in such a manner that it pressed with its edge against the two iron plates suspended by wires to the contrary poles. I may add that, in order to produce a better contact between the two plates of iron and the glass plate, I fitted pieces of wood between the sides of the trough and the external surfaces of the two plates, to keep them constantly pressed against the glass plate. After two days of voltaic action, metallic iron was deposited on the plate suspended to the negative pole in vertical bands parallel to the two sides of the edge of the glass plate, a ridge alternating with a furrow. The hollows corresponded to the space occupied by the edge of the glass plate, and the reliefs to the sides of the same plate. The hollow lines (those, that is to say, in which no metallic iron was deposited) were therefore *nodal lines*, and the lines on which the iron was deposited were lines of vibration or *segments*. They might have been the strings of a harp manufactured in the mysterious silence of the molecular recesses.

Instead of a straight glass I substituted an S-shaped one, so that the line formed by the contact of the glass upon the iron was curved. I thus obtained a curvilinear deposit of iron with alternate raised and depressed curved lines. But the curved lines were neither so sharp nor so well defined as the straight ones, because the terminal section of the badly curved plate was not all in one plane, and a considerable part was not in contact with the iron plate. The current, moreover, was weakened and the bath a little exhausted, which must have had some influence on the want of sharpness of the nodal and the vibrating lines.

The uniform pressure of a glass plate has been sufficient to render inert entire spaces of iron, so as to prevent any deposition on them. If this is the case with right and with curved lines, it cannot be doubted that, by making designs in glass (and perhaps in clay or porcelain), all the parts in contact with the edge of the design would be preserved from metallic deposits. It is probable that the same design would be reproduced on the same surface a greater number of times, according as the space left free by the pressing surfaces were more extended.—*Comptes Rendus*, October 7, 1867.

Sulph

N₂HO₂

tic Ether CH³H⁴I²

Chloride of Phosphoru

1·100

Lin

omine H²C

Line of pressure of 10ᵐᵐ
Dᵒ of 9ᵐᵐ
Dᵒ of 8ᵐᵐ

7ᵐᵐ
6ᵐᵐ
5ᵐᵐ
4ᵐᵐ
3ᵐᵐ
2ᵐᵐ
1ᵐᵐ

Alcohol (line of dynamic observations below 760ᵐᵐ pressure)

WATER (Line passing through 30° 40° 50° 60° 70° & 100° of Courbe graphique)

(H°C. HO½)
(HO½)

Series II, p.509. Vol. I Regnault. (Mem. Inst. Vol. XXI) Series C. p.507

S°O°½ + 18(HO½)
S°O°½ + 10(HO½)
S°O°½ + 8(HO½)
S°O°½ + 6(HO½)
S°O°½ + 5(HO½)
S°O°½ + 4(HO½)
S°O°½ + 3(HO½)
S°O°½ + 2(HO½)

Line of pressure 1ᵐᵐ

Scale for laying off values of $\sqrt[4]{\frac{p}{n} \cdot \frac{T}{274^\circ}}$

0·600
0·550
0·500
0·450
0·400
0·350
0·300
0·200
0·150
0·100

-80° -70° -60° -50° -40° -30° -20° -10° 0° Temperature 10° Centigrade 20° Scale -30° -40° -50°

2·45

2·00

Transition points of W. & Alcohol

Chloroform

Chloride of Phosphorus

uir
of Plate IV
7 of Plate IV

1·00

-274°

Line of

Avogadro's Mercu

0

Line of 5

0·10
0·20
0·30
0·40
0·50
0·60
0·70
0·80
ETHER
NODE
0·90
1·00
1·10

350°

1·20   *urt R*
1·30
1·40
1·50

Lines of Saturated Vapour Density
from the Observations of M. Regnault (except those marked W)

The dark part is the Range of observation that determined the line.
The crossed part of five of the lines shew range of Liquid expansion observations
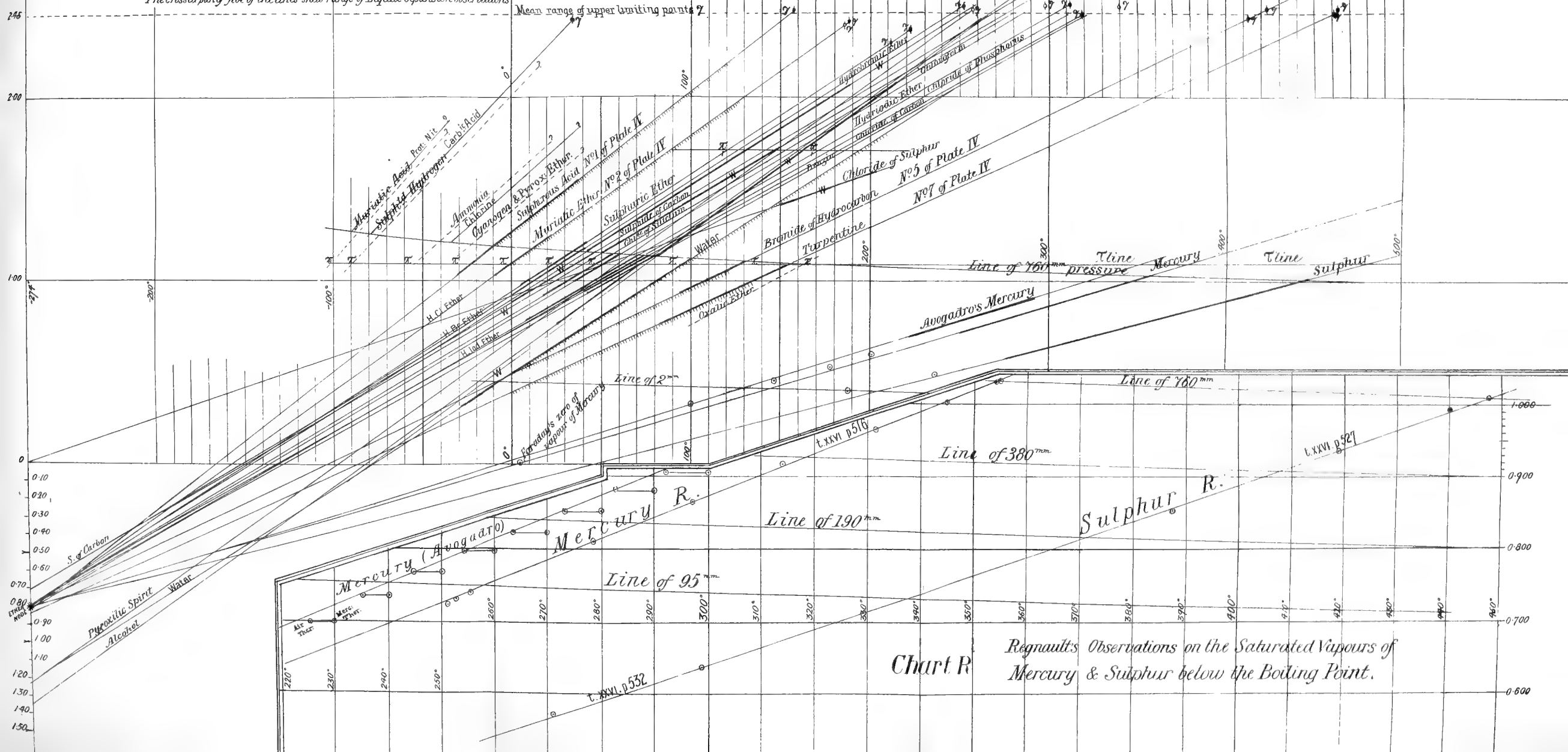
Chart R.

Regnault's Observations on the Saturated Vapours of
Mercury & Sulphur below the Boiling Point.

Chart Q see § 32
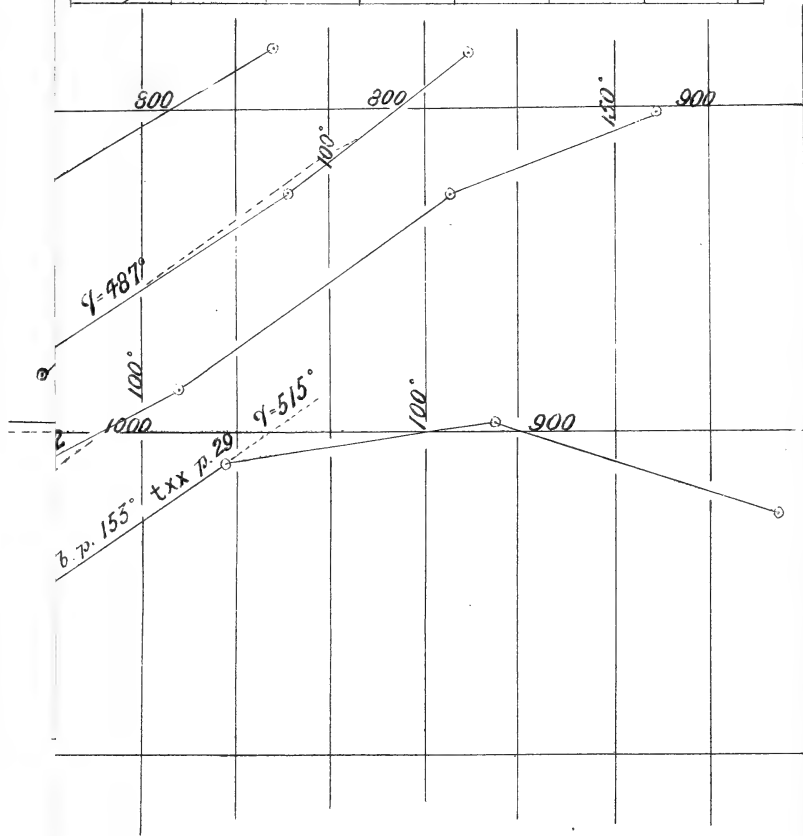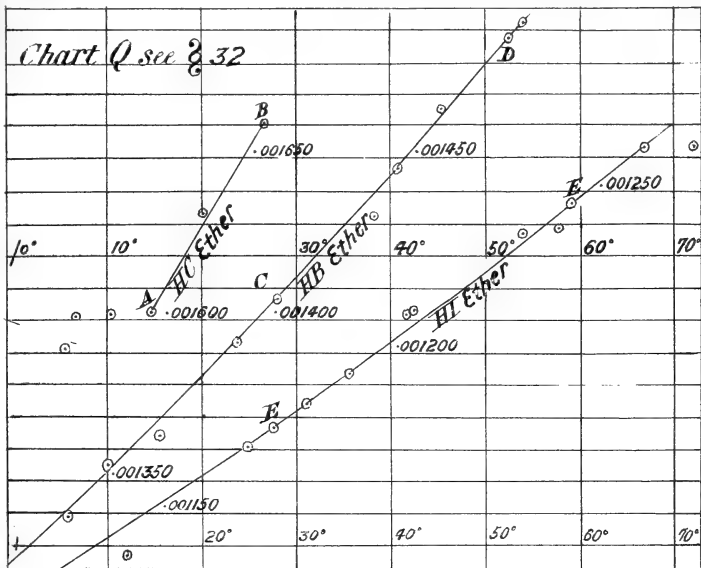
Lines of Liquid Expansion (see § 31)

Nº1. Sulphurous Acid
 2. Muriatic Ether } M. Drion.
 3. Amylic Alcohol
 4. Bromide of Amyle
 5. Bromide of Hydrocarbon
 6. Sulphurous Ether
 7. Turpentine

Nº8. Liq: Holl: Trichlor:
 9. Protochlor: Arsenic
 10. Protobromide of Phosphorus
 11. Bromide of Siliciam
 12. Protochloride of Carbon
 13. Formic Ether

Chart Q see § 32

.001650 .001450
E .001250
Iº Ether 30º Ether IIB Ether
.001600 .001400 III Ether
.001200
.001350
.001150

Nº12 CCl⁴ b.p. 124° t.xxxiii p.258 7=298°.7
Nº13 CH³HO²+O⁴ CH – b. p. 163° t.xv p.383 7=303°.2

No 1 & 2 are M. Drions Observations; the radius of wt are marked at the respective points

Nº1 S O²
Nº2 CH²H⁵Cl⁴ b.p. 122° 7=167° t.xvi p.35
Nº3 C²⁴ H⁵ HO²⁴ b.p. 132° 7=184°.7 t.xxvi p.21 7=287° t.xIX p.198

Nº4 C²⁴ H⁵ H³ Br² b.p. 118° 7=345° t.xxxiii p.221 7=440°
Nº5 CH²Br b.p. 13° t.xx p.41
Nº6 C²H⁴ HO²⁴ S²O b.p. 160° t.xx p.344 7=463° t.xx p.16 7=487°
Nº7 C⁵H⁵ b.p. 157° t.xxiii p.235 7=46°
CH²Cl²⁴ b.p. 153° t.xxxiii p.228 7=515°
Nº8
Nº9 As⁴ Cl²⁴ b.p. 134° t.xx p.12
Nº10 P⁴ Br b.p. 175° 7=580°
Nº11 Si Br² b.p. 153° t.xx p.29

Maximum Divergence a(√1/3)
Maximum Divergence

XIX. *On the Velocity of the Propagation of Waves in Gaseous Media.* *By* V. Regnault[*].

THE formulæ which physicists have hitherto employed to represent the rate of propagation of a wave in a gaseous medium which is either unbounded in all directions, or enclosed in a straight cylindrical tube, assume the gas to be perfectly elastic, and the excess of the elastic force which gives rise to the propagation of the wave to be infinitely small in comparison with the elasticity of the medium at rest.

These hypotheses, being introduced from the first into the calculation, necessarily produce their consequences in the resulting formulæ; but as not one of the known gases exactly satisfies these conditions, we may expect to find sensible discrepancies between the results of actual experiments and those deduced by calculation from theory.

In fact, when we assert that a gas is perfectly elastic, we assume :—

(1) That it exactly obeys Mariotte's law. Experiment, however, shows that all gases deviate more or less from this law.

(2) That its elasticity is not affected by surrounding objects. But my experiments on the propagation of waves in tubes show that the walls of the tubes exert a very notable influence.

(3) That the gas does not oppose any *inertia* to the transmission of the wave. Now my experiments show that the emission of a strong wave always causes a true displacement (*véritable transport*) of the first gaseous layers, which displacement considerably increases the velocity of the wave's propagation, especially through the first portion of its course.

(4) In order to make allowance for the acceleration produced by the sudden disengagement of heat which takes place at the moment of the wave's passage, Poisson's law is introduced into the calculation. But this law is only exact if the gas has perfect elasticity, if it obeys Mariotte's law, &c.

Finally, the theoretical calculation assumes that the excess of compression which exists in the wave is infinitely small compared with the barometric pressure supported by the gas. But the experiments made to determine the rate of sound in free air have been hitherto made by means of a cannon, and the wave has been reckoned from its source, namely the cannon's mouth. Now this wave as it leaves the cannon is under enormous compression—a compression, it is true, which diminishes very rapidly as the wave spreads spherically through space; but during the first part of its course it cannot be supposed that its compression is *infinitely small*.

When the excess of compression in the wave is a sensible fraction of the compression of the gaseous medium at rest, we can no longer employ Laplace's formula, but must have recourse to a more complex formula embracing the true elements of the problem. Even the formula which I have given in my Memoir is only an approximation; for it implicitly admits Mariotte's law and all its consequences.

In short, the mathematical theory has as yet only touched upon the propagation of waves in a *perfect gas*—that is to say, in an *ideal fluid* possessing all the properties which had been introduced *hypothetically* into the calculation. It is therefore not surprising that the results of my experiments often disagree from theory.

I. According to theory, a plane wave in a straight cylindrical tube should advance to an indefinite distance with a constant velocity. My experiments show that the intensity of such a wave continually diminishes, and this the more quickly the less the section of the tube employed.

In order to establish this fact conclusively, I created waves of equal intensity by discharging one gramme of gunpowder from the same pistol at the orifices of conducting tubes of very different sectional areas, and I endeavoured to ascertain the length

necessary to be traversed for the explosion to become inaudible. I have further endeavoured to measure the much longer path, at the end of which the inaudible wave ceases to give any indication upon the most sensitive membranes* which I have used. I have thus found that:—

(1) In a gas-pipe at Ivry, having the internal diameter of 0·108 metre, the explosion is heard at the other end at a distance of 566·7 metres, but the sound is very faint. If the further extremity be hermetically closed with a piece of sheet iron, and if the ear be placed at the end where the pistol was discharged, it requires the utmost attention to catch the sound of the return wave. So that in a straight cylindrical tube of 0·108 metre internal diameter a length of 1150 metres is sufficient to extinguish entirely the sound produced by the discharge of a pistol containing one gramme of powder.

(2) In a gas-pipe in the *Rue militaire,* 0·30 metre in diameter, the discharge of the pistol is heard very clearly at the other end at a distance of 1905 metres. If this end be closed by a sheet of iron and the ear be applied to the end where the discharge takes place, the reflected wave is indeed heard, but with extreme difficulty. In this case the wave has traversed in the pipe a distance of 3810 metres.

(3) In the great pipe of the St. Michel sewer†, of 1·10 metre diameter, the wave produced by the discharge of the pistol gives an intense sound when it reaches the other end B after having travelled 1590 metres. After one reflexion at B it returns to the point A, whence it started. Its entire path has then been 3180 metres. Its sound is found to be weakened, but it still has sufficient intensity to be heard outside without there being occasion to remove the membrane‡ which closes the opening A. After a

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* As stated by the author, the details of the experiments are still unpublished; reference is, however, made to them in this *Compte Rendu.* Judging only from what is herein stated, it appears to the translator that, for detecting and measuring the velocity of inaudible waves, the author closed one or both of the ends of his tubes with elastic thin iron plates (membranes) which marked or were marked by strips of blackened paper passing with uniform velocity over them. It does not appear whether the marking was continued while the air in the tube was at rest, and ceased at the moment of the arrival of the wave, or whether the mark was only made when the wave arrived. In either case, of course, the length of the strips of paper between the successive marks (or interruptions of marking) would be measures of the velocity of the wave. This suggested explanation of what might perhaps otherwise not be clear is, of course, only made under correction.—F. G.

† "*Dans la grande conduite, du diamètre de* 1·10 *mètre de l'égout Saint Michel.*" I suppose this is a gas-pipe (certainly enormous) laid in a sewer. Is it the sewer itself? It does not much matter.—F. G.

‡ Probably a thin metallic plate. In this case it appears that both ends of the tube are closed.—F. G.

M 2

second reflexion at B and a second return to A, the wave has travelled 6360 metres; the percussion is still heard very distinctly. Finally, it is only after another reflexion at B that the third return to A becomes inaudible, and perfect silence reigns in the tube.   The entire course is then 9540 metres.

7 Thus the discharge in a pistol of 1 gramme of powder gives a vibration in the air (*son*) which becomes inaudible when it has traversed

1150 metres in a tube of the diameter 0·108 metre.
3810   „   „   0·300 „
9540   „   „   1·100 „

These lengths are sensibly proportional to the diameters.   It is nevertheless probable that the path would be longer were not the wave subjected to successive reflexions which continually diminish it.

When the wave has no longer sufficient intensity to produce the sensation of sound upon the ear, or when it has been *so far modified* as to be unable to do so, it may nevertheless, even after a very prolonged course, still mark its arrival upon the membranes.

Thus when the wave is produced by a charge of 1 grm. of powder, it makes its last impression upon a membrane when it has passed over the following courses:—

4056 metres in a tube of diameter 0·108 metre.
11430   „   „   0·300 „
19851   „   „   1·100 „

But in a pipe of 1·100 metre diameter, which forms the grand service-pipe of Villemonble, I have observed paths of much greater length,—the charge of powder, it is true, being raised in this case to 2·40 grms.   Thus in the Table showing the results of one of the series of experiments made with this large tube, the last mark corresponds to a wave which had traversed 58641 metres ; and if the bands of paper were allowed to remain, it was easy to detect as many as ten returns of the wave to the membrane A.   This is, in effect, a path equivalent to 97735 metres, or nearly 100 kilometres ; but the bands of blackened paper were then so long that I found it impossible to collect the indications of more than six returns ; the band of paper with this number had already reached the length of 27 metres.

What are the causes which thus weaken a plane wave when it is propagated in a straight cylindrical tube ?   They are of several kinds ; but the chief one undoubtedly depends upon the continual loss by the wave of a part of its *vis viva* by the reaction of the elastic sides of the tube.   This is shown distinctly in the great tube of the *Saint Michel* sewer, which is supported

upon iron columns in a large vaulted gallery. When the wave
first passes, a very loud noise is heard outside, in whatever part
of the course the observer is situated. Consequently a consi-
derable part of the *vis viva* is thereby scattered abroad. The
same takes place at the extremities and at all the openings fur-
nished with membranes. This loss necessarily continues after
the wave has ceased to have sufficient intensity to affect the ear;
and it is, strictly speaking, sufficient to explain why the sound
becomes extinguished, and how the wave becomes so enfeebled
as no longer to disturb the most sensitive membranes. But I
do not think that this is the only cause at work. There is
another which arises from an action of the solid wall upon the
gas, whose elasticity it sensibly diminishes. I shall give a proof
of this immediately.

II. Laplace's formula does not contain the expression of the
intensity of the wave. According to this formula the rate of
propagation of a wave is the same, whatever its intensity may be.
But according to the more general formula which I have given,
this velocity should be greater the greater the intensity of the
wave. Now we have just seen that in a straight cylindrical tube
the intensity of the wave does not remain constant as has been
hitherto supposed, but that it diminishes continually, and this
the more rapidly the smaller is the section of the tube. The
necessary consequence of this is that the rate of propagation
of a wave in a tube ought continually to diminish as the wave
advances; and this diminution should be the more rapid the
smaller is the section of the tube. This is, in fact, what occurs
in all my experiments. I shall confine myself here to the dis-
cussion of the mean velocity of a wave produced by the discharge
of a pistol, and which travels through dry air at $0°$ C., such a
wave being measured from its commencement up to the moment
when it ceases to be of sufficient intensity to affect the mem-
branes. I select from experiments made upon tubes of the dia-
meters $0·108$, $0·300$, and $1·10$ metre.

(1) Tube of diameter $0·108$ metre (*Route d'Ivry*).

Distances traversed.	Mean velocities, V'_0.	Distances traversed.	Mean velocities, V'_0.
Charge of powder $0·3$ grm.		Charge of powder $0·4$ grm.	
metres.	metres.	metres.	metres.
566·74	330·99	1351·95	329·95
1133·48	328·77	2703·00	328·20
1700·22	328·21	4055·85	326·77
2266·96	327·04	5407·80	323·34*
2833·70	327·52		

* This last velocity, being indicated on only one band, is perhaps not
exact.

The diminution of the mean velocity of one and the same wave reckoned from its origin, but which is examined after traversing longer and longer paths, is very marked. ⨉ End

(2) Tube of diameter 0·33 metre (*route militaire*).

Distances traversed.   Mean velocities, V'_0.

Charge of powder 0·4 grm.

metres.	metres.
1905.0	331·91
3810·0	328·72

Charge of powder 0·4 grm.

1905·0	332·37
3810·0	330·34

Charge of powder 1·5 grm.

Reflexion on the closed end B.

3810·3	332·18
7620·6	330·43
11430·0	329·64
15240·0	328·96

The mean velocities for waves produced by the same charge of powder and for equal paths are accordingly much greater in a tube of 0·30 than in one of 0·108 metre diameter.

(1) Tube of diameter 1·10 metre (*égout St. Michel*).

Distances   Mean
traversed.   Velocities, V'_0.

Charge of powder 1·0 grm.

metres.	metres.
749·1	334·16
920·1	333·20
1417·9	332·50
2835·8	331·72
5671·8	330·24
8507·7	330·87
11343·6	330·68
14179·5	330·56
17015·4	330·50
19851·3	330·52

The mean velocity of propagation in the tube of diameter 1·10 metre diminishes less quickly than that in the one of the diameter 0·30. The first velocities are greater, because they are taken much nearer to the origin of the wave.

The differences are still more marked when we compare the

mean limiting velocities in the three tubes—that is to say, those velocities which correspond to a wave sufficiently enfeebled from its commencement as no longer to affect the membranes.

These limiting velocities were found to be :—

	metre.	metres.		metres.
In the tube of diameter . }	0·108	$V'_0 = 326·66$	Dist. traversed	$= 4055·9$
,,	0·300	$V'_0 = 328·96$	,,	$= 15240·0$
,,	1·100	$V'_0 = 330·52$	,,	$= 19851·3.$

In these experiments the wave was produced by the same charge of powder. The membranes are the same, and have therefore the same sensitiveness ; in other words, they ought to cease to indicate in the three tubes when the waves have acquired the same feebleness. If the weakening of the wave arose entirely from the loss of *vis viva* through the walls of the tube, the mean limiting velocity should be the same in the three tubes, because the wave has the same intensity in all three cases, both at its origin and at the moment when it makes its last impression upon the membrane. These limiting velocities being, on the contrary, very different, we must conclude that the walls of the tube exercise upon the enclosed air another action besides the action which we have just pointed out, which considerably diminishes its elasticity without sensibly changing its density. In consequence of this the *velocity of propagation of a wave of the same intensity in straight tubes is less according as the section of the tube is less.*

It is probable that the nature of the wall of the tube (its more or less perfect polish) exerts an influence upon this phenomenon. I may mention a fact which proves it. In the Paris sewers of great diameter the workmen are usually signalled to by sound of trumpet. It is observed that the signals are carried incomparably further in galleries whose walls are covered with smooth cement than in those lined with rough stonework.

In order that this action of the walls upon the elasticity of the gaseous medium may be absolutely nothing, the diameters of the tubes must be infinite ; in other words, the propagation of the sound must take place in the open air. But the action of the walls must be very small in the great tube of 1·10 metre diameter. I have assumed that it is nothing ; and I have concluded from my numerous and very concordant experiments, that the mean rate of propagation in dry air at zero of a wave produced by the discharge of a pistol and reckoned from the muzzle of the pistol to where it becomes so weak as to cease to affect the most sensitive membranes, is

$$V'_0 = 330·6 \text{ metres.}$$

I have also endeavoured to determine the velocity of the weak-

est wave, the velocity which I call the minimum velocity (*vitesse minima*). This determination could only be made with any precision in the wide tubes of 1·10 metre diameter. It was found that

$$W'_0 = 330·30,$$

a value which differs very little from the *mean limiting velocity*.

In tubes of smaller diameter the minimum velocity is still less.

III. When the wave is produced, not by the sudden explosion of a detonating mixture, but by the injection of a small quantity of air more or less compressed, its velocity of propagation in the same tube is greater when the intensity is greater; so that the velocity of such a wave, like that caused by the discharge of a pistol, diminishes continually.

In the tube of 1·10 diameter the waves produced by the injection of compressed air have sensibly the same initial velocity of propagation as those caused by the discharge of the pistol; but their mean limiting velocity is a little less. The same fact appeared in a tube of 0·30 metre diameter when the excess of the pressure of the injected air was sufficiently great.

IV. The behaviour is the same of the wave produced by the sudden closing of the orifice on striking it with a disk moving at a great rate. *The velocity of propagation diminishes sensibly according as the path increases.* This is shown very clearly by experiments made by means of a piston impinging upon a tube 0·216 metre diameter (*la route Choisy-le-Roi*). In the great tube of 1·10 diameter which forms the service-pipe of Villemonble, the mean rate of propagation, in the same path of 9773·5 metres, was found to be

$V'_0 = 333·11$ metres when the sound is produced by a pistol.
$V'_0 = 332·56$,,   ,,   an impinging piston.

So that the wave caused by the piston travels a little slower than that caused by the discharge of a pistol; but this is entirely due to the less intensity of the former. The wave caused by the piston never gave any indication on the membrane of a second return which would correspond to a distance traversed of 19547 metres, while the wave caused by the pistol never failed to indicate frequent returns.

V. The experiments which I have made upon the waves produced by the human voice and by wind instruments are described in detail in my Memoir: the description of them would be too long for this extract.

VI. Our theoretical formulæ of the velocity of sound in air do not take into account the barometric pressure to which the air is subjected. If these formulæ are exact, it would follow that *the velocity of a wave in a gas is the same whatever be the pressure to*

which the gas is submitted. The only direct experiments which can be here cited in confirmation of this law were made in the open air. They are those of HH. Stampfer and Myrbach in 1822 in Tyrol, between two stations having a difference of level of 1364 metres, and those of MM. Bravais and Martens, performed in Switzerland in 1844, at two stations whose difference of level was 2079 metres. Unfortunately the mean barometric pressures which the air suffers at the two places does not differ sufficiently from the pressure at the level of the sea.

I have, in my Memoir, given two series of experiments to determine the velocity of propagation of sound in the air when under various pressures, and contained in tubes of 0·108 metre diameter.

The first experiment was made with the gas-pipe of the *route militaire* near Ivry, having the length of 567·4 metres. The pressures varied from 0·557 to 0·838, and the consequent densities of the air from 1·0 to 1·5.

The second experiment was made in a little horizontal tube in the court of the Collége de France, the length of the tube being only 70·5 metres. The pressures varied from 0·247 to 1·267; consequently the density of the air varied from 1 to almost 5.

It was not possible to establish any sensible difference in the rate of propagation of sound in air under these very different pressures. My experiments accordingly confirm the exactness of the law which I have just enunciated.

VII. If we compare V and V_1 (the velocities of the same wave in two different gases having the same temperature and being under the same pressure), and if further we assume that they obey Mariotte's law, that they have the same coefficient of dilatation, that they satisfy Poisson's law, &c., in short that they are perfect gaseous media, we ought, according to theory, to have*

$$\frac{V'}{V} = \sqrt{\frac{d}{d'}}.$$

So that, if one of the gases is atmospheric air, and if δ represents the density of the other gas compared with air, we have

$$\frac{V'}{V} = \sqrt{\frac{1}{\delta}}.$$

Hitherto no direct experiment has been made to determine the rate of propagation of a wave in any other gas than atmospheric air. Attempts have only been made to prove the exactness of the above law in an indirect way, founded on the theory of sonorous tubes.

* d and d' being the respective densities of the gases.—F. G.

In my Memoir I give two series of direct experiments upon those gases which I have been able to prepare in sufficient quantity.

The first series was made upon the tubes of 0·108 metre diameter in the *route d'Ivry*, the available length of which is 567·4 metres. This tube I was able to fill successively with hydrogen, carbonic acid, and coal-gas.

For the second series, I made use of the little tube in the Collége de France, which has the same section but a length of only 70·5 metres. I was able to use this tube for carbonic acid, protoxide of nitrogen, and ammonia. In the following Table the results obtained by means of both the tubes are thrown together.

$$\frac{V'_0}{V}.$$

	Tube of length 567·3 metres.	Tube of length 70·5 metres.	$\sqrt{\dfrac{1}{\delta}}.$
Hydrogen	3·801	. . . .	3·682
Carbonic acid . . .	0·7848	0·8009	0·8087
Protoxide of nitrogen .	. . . .	0·8007	0·8100
Ammonia	. . . .	1·2279	1·3025

If we compare the ratios $\frac{V'}{V}$ of the first two columns with the calculated values of $\sqrt{\dfrac{1}{\delta}}$, we find a rather remarkable coincidence. The differences would certainly have been less if the experiments could have been performed on pure gases; but this is very difficult in tubes of such great capacity. Further, the values of $\sqrt{\dfrac{1}{\delta}}$ are not very exact, because we are often obliged to take the theoretical density of the gas with regard to air, and not its actual density, which is the only one really concerned.

My experiments show that we may accept the law $\frac{V'}{V} = \sqrt{\dfrac{1}{\delta}}$;

but only as a *law true in the limit* (*loi limite*), a law which gases would exactly satisfy if they were placed under circumstances where they would behave as perfect gaseous media.

VIII. My experiments for the determination of the rate of propagation of waves in the open air were made by the method of reciprocal cannon-reports. It is clear that at its commencement the wave has a very great intensity; but this diminishes very quickly as the wave spreads through space. Further, at the moment of the explosion of the cannon the layers of air next to the cannon undergo a true displacement which still further increases the velocity of the propagation. Thus, in consequence

of this transport and of its great intensity, the wave advances more quickly, especially in the direction of the line of fire in the first portions of its course than in the following ones. But this acceleration quickly diminishes, and becomes almost insensible when the wave traverses great distances.

Two series of experiments may be distinguished. In the first series, embracing eighteen reciprocal discharges from cannon, each cannon was placed about 1280 metres from the membrane which indicated the arrival of the wave. We find for the mean velocity of propagation in calm dry air at 0° C.,

$$V'_0 = 331 \cdot 37 \text{ metres.}$$

In the second series each cannon was distant about 2445 metres from its corresponding membrane. This series embraces the experiments during eleven days, consisting of 149 reciprocal discharges of cannon, the conditions of temperature and wind being very various.

The general mean for the velocity in calm dry air at 0° C. is

$$V'_0 = 330 \cdot 7 \text{ metres.}$$

This velocity is sensibly less than that of the first series. We accordingly again find here that the velocity sensibly diminishes as the path increases.

In the second series the temperature varied from 1°·5 to 21°·8 C. I deduce from this that the correction for temperature which is usually received is the true one.

IX. These researches on the propagation of the wave in gaseous media were undertaken from the dynamical point of view of the theory of heat. I believe that important deductions may be made in this respect; but the space at my disposal for this extract prevents me from developing them.

XX. *Researches in British Mineralogy.*
By DAVID FORBES, *F.R.S. &c.*[*]

II.

Polytelite[†].

LOCALITY: Tyddynglwadis silver-lead mine in the valley of the river Mawddach, about six miles above Dolgelly, North Wales.

[*] Communicated by the Author.

[†] Remarks having been made on the employment by me of "the rarely used name Polytelite" instead of the uncouth German one Weissgiltigertz or Weissgültigerz, I may explain here that, in adopting a name long ago proposed by Glocker (and accepted by several other mineralogists) for such argentiferous tetrahedrites as are specially characterized by so notably large

When examining this district in May 1867, the attention of the author was directed by Mr. Ezekiel Williamson to the presence of small particles of a mineral occurring disseminated in the lead ores of this mine, and which he supposed to be the variety of tetrahedrite found in Wermland in Sweden, called by Svanberg aphthonite. For comparison, Svanberg's analysis* is here extracted :—

Copper	.	.	.	32·910
Zinc	.	.	.	6·408
Silver	.	.	.	3·094
Iron	.	.	.	1·313
Cobalt	.	.	.	0·491
Lead	.	.	.	0·043
Antimony	.	.	.	24·770
Sulphur	.	.	.	30·049
Arsenic	.	.	.	1·292
Rock	.	.	.	trace
				100·370

On comparing the Tyddynglwadis mineral, however, with a specimen of the aphthonite from Wermland, the external characters differed so considerably as to lead to the inference that it was not this mineral, but some other variety of polytelite.

Unfortunately it was found quite impossible to obtain the mineral sufficiently free from the associated galena to enable confidence to be placed either in the determination of its specific gravity or exact chemical composition. The fact, however, of its being a true polytelite was satisfactorily proved by the assays of Mr. Williamson, which showed that the percentage of silver in the mineral, as free from extraneous matter as possible, amounted to 11·25 per cent.

The minerals which have been discovered occurring in this lode associated with the polytelite are as follows :—Native gold, native

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a percentage of silver as to cause metallurgists to regard them as silver ores properly so termed, when distinguishing them from the so-called argentiferous copper ores, I have done so in accordance with the views expressed by Dana, in his paper " On System in Mineralogical Nomenclature" (American Journal of Science and Arts, vol. xliv. p. 145, September 1867), and because I further consider this name a convenient one for distinguishing these varieties of the mineral species tetrahedrite, for which we have no other distinctive English name,—since the expression "argentiferous grey copper ore or tetrahedrite " merely intimates the presence of silver (which is very rarely, if ever, altogether absent from any tetrahedrite), but does not indicate that this metal enters as an important constituent into the composition of the mineral itself.

* *Öfvers. Kongl. Vet. Akad. Förhandl.* 1847, vol. iv. p. 87.

silver, galena, chalcopyrite, blende, iron pyrites, arsenical pyrites, and quartz. It may be stated here that the crystallized galena in immediate proximity to the rich polytelite contained upon assay only 0·08 per cent. of silver.

The geological position of this mineral lode is close to the junction of the Cambrian rocks with the Lingula-beds of the Lower Silurian formation. The main lode runs nearly N.W. and S.E., dipping to N.E., and cuts through the Menevian group with its associated diabases : the *Paradoxides Davidis* is found in abundance in the slates within a few yards of the outcrop of the lode.

Before concluding this notice of the occurrence of polytelite in Wales, it may not be out of place to add here a few lines on the importance of such an inquiry when considered from a practical or economical point of view.

Upon reading the report of the proceedings of a meeting of the Tyddynglwadis Mining Company in 1864, a statement will be found, in the agent's report of "surface" operations (p. 15), to the following effect :—" Our slime-pits are very deficient. I would strongly recommend your attention here, because some of these slimes are very rich in gold and silver : the lightest slime, curiously enough, is always the richest in the precious metals." The perusal of this paragraph at once gave rise to the suspicion that the bad results obtained from the dressing-machinery and operations employed by the Company in the treatment of the ores of this mine might in part at least be due to the silver being mainly present in the ore in the state of polytelite (specific gravity about 4·8), and not, as previously supposed, contained in the galena (specific gravity 7·7). This suspicion, corroborated by the small percentage of silver found, as before stated, in the pure galena crystals when assayed, was still further confirmed by the result of the following experiment.

A portion of the ore, mainly consisting of galena with quartz and a talcose mineral, along with some minute specks of iron pyrites, polytelite, blende, and chalcopyrite, was pulverized, and by the use of a sieve brought to a very uniform powder, which was then carefully washed in a small batea until it was divided into two portions of different specific gravity.

The most metallic-looking and heavier of these two products appeared on inspection to consist mainly of clean galena, whilst the lighter or more earthy portion would contain all the other substances present in the ore.

This latter was now submitted to a similar washing, using even more care in so doing than in the former case, and by this means was in its turn subdivided into two products. The smaller or heavier and more metallic portion, when examined with a mag-

nifier, consisted of polytelite, along with some little galena and considerable amount of iron pyrites, blende and copper pyrites, and a little quartz sand; whilst the lighter or earthy portion consisted chiefly of quartz and rock débris, along with some few specks of polytelite, copper and iron pyrites, and blende.

The assay of these three ultimate products of this experimental washing now showed the distribution of the silver as follows:—

(1) The heavier or argentiferous galena, which corresponded to the dressed ore obtained on the large scale in the Company's operations contained 60 ounces of silver per ton, along with about 80 per cent. of lead. On the large scale it is stated, in the before-mentioned report, that the results varied from 55 to 78 per cent. of lead, along with from 45 to 53 ounces of silver per ton washed ore.

(2) The less dense metallic part, which evidently contained most of the polytelite, and the greater part of which would, in the ordinary process of washing on the large scale as adopted at Tyddynglwadis, have been carried away and lost, was far richer than the preceding, and contained 182 ounces of silver to the ton, with a little lead and more copper and zinc.

(3) The third product consisted of the lighter non-metallic particles, chiefly quartz and rock débris, along with traces of the lighter metallic compounds, and only contained a mere trace of silver.

Sulphide of Iron and Nickel.

Locality: nickel mine in the woods above Inverary Castle, Argyleshire; the mineral occurring in a lode running nearly east and west with a dip of about 42° to the north, which traverses the metamorphic slates and schists.

The characters of this mineral were as follows:—massive; fracture between granular and semicrystalline; brittle; opake; lustre metallic; colour light bronze-brown; streak greyish black; powder bronze-brown; hardness 3·5, scratching calcite but not fluor-spar; strongly magnetic. Specific gravity 4·50 at 60° F. After some time, on exposure to the air the mineral crumbles to pieces, some specimens breaking up after a few months, whilst others have resisted as many years.

Heated in a closed tube it remains unchanged, but occasionally shows traces of a sublimate of sulphur on the sides of the tube, which possibly may be due to the presence of an admixture of iron pyrites. Heated in an open tube it evolves sulphurous acid.

On charcoal alone it does not decrepitate, but fuses readily to a globule, which upon breaking possesses a bronze-yellow fracture and metallic glance. When this globule is treated with borate in the oxidating-flame, it by degrees gives up all its iron

to the borate, and, if the treatment is prolonged, ultimately leaves a globule of nearly pure disulphide of nickel ($Ni^2 S$), which gives the reactions for nickel when further treated with borate in the oxidating-flame; any copper present in the mineral remains in this disulphide. The mineral, if calcined on charcoal in the oxidating-flame at a heat below its fusing-point, reacts for nickel and iron when treated with borate. The cobalt was found to be present in so small quantity in the specimen analyzed, that its reactions were quite overpowered by those of the nickel and iron, and it could not be detected until a special search for it was made by Plattner's arsenical process.

The qualitative analysis showed the presence of sulphur, iron, nickel, traces of copper and cobalt, along with a little rock-matter, which consisted chiefly of quartz, but which contained some magnesia in the form of a silicate easily decomposed by acids.

The quantitative analysis was conducted as follows :—A weighed quantity was dissolved in nitrohydrochloric acid, which left a small amount of insoluble matter, along with some free sulphur, which was estimated by the loss found on igniting the insoluble matter. The solution (having previously been evaporated to drive off any large excess of acid) was now precipitated by chloride of barium, and the resulting sulphate of barytes determined. The sulphur calculated from the weight of this sulphate of barytes, in addition to the amount of free sulphur previously found, gave the total amount of sulphur present in the mineral.

The nickel and iron in the filtrate were separated by carbonate of barytes, and the iron in the precipitate determined, as usual, as sesquioxide. The solution containing the nickel, along with a little magnesia, was first precipitated by sulphuric acid in order to remove the excess of the baryta, which was filtered off, and then the nickel was precipitated by colourless sulphide of ammonium with the usual precautions. This sulphide was, after incineration, dissolved in nitrohydrochloric acid, and the oxide precipitated by caustic potash boiling. Upon examination, only a trace of cobalt was found present in this oxide. In the solution from which the sulphide of nickel had been separated, the magnesia, after removal of the excess of baryta by sulphuric acid, was thrown down as phosphate of ammonia and magnesia, and determined as pyrophosphate of magnesia as usual.

20·07 grs. mineral afforded 0·52 gr. free sulphur, 0·05 gr. insoluble matter, 51·53 grs. sulphate of barytes, 14·30 grs. sesquioxide of iron, 2·85 grs. protoxide of nickel, and 0·54 gr. pyrophosphate of magnesia ; and from these results the percentage composition is calculated to be as follows :—

Sulphur	37·50
Iron	49·97
Nickel	11·17
Cobalt and copper .	traces
Magnesia	0·96
Insoluble matter .	0·24
	99·84

Subtracting the amount of insoluble matter and magnesia and dividing the loss equally on the remaining constituents, we have the percentage composition as follows:—

Sulphur . .	37·50	38·01
Iron . . .	49·97	50·66
Nickel . . .	11·17	11·33
	98·64	100·00

Considering the nickel to be present in this mineral in the state of protosulphide (which is probable, both as that compound is known in the mineral kingdom in the pure state as Millerite, and also as, in the Gap mine, Lancaster county, Pennsylvania, Millerite is occasionally found in the nickeliferous pyrrhotine which forms the object of the exploration), the exact state of sulphuration of the iron is still somewhat uncertain; for whilst some mineralogists have regarded this mineral as being merely a protosulphide of iron in which the iron is in part replaced by the nickel, the larger amount of sulphur shown in this and many other analyses, as well as the strongly magnetic properties of the mineral, appear to indicate the probability of the iron being really present as pyrrhotine or magnetic sulphide of iron ($Fe^7 S^8$). Taking both these views into consideration, the following percentage composition would approximate to the numbers found experimentally:—

	$5FeS+NiS.$	$5(Fe^7 S^8)+NiS.$
Sulphur . .	36·16	37·18
Iron . . .	52·73	51·89
Nickel . . .	11·11	10·93
	100·00	100·00

Some have supposed that these ores may be a mere mixture of pyrrhotine with more or less Eisennickelkies; but as this latter species is stated by its discoverer, Scheerer, to be non-magnetic, a property which he made use of in order to obtain it free from the strongly magnetic nickeliferous pyrrhotine which accompanies it *in situ*, the Inverary mineral, picked as clean as possible, was pulverized and then treated with a magnet in order to see whether any non-magnetic particles of Eisennickelkies would remain be-

hind. This was not found to be the case; the mineral, although not crystallized, appeared to the eye (and when magnified also) to be perfectly homogeneous, and did not in any way convey the impression to the examiner of being a mixture. Moreover several other specimens, not only from this mine but from another mine at Craigmuir, about to be referred to, and also from a mine in Norway, possessed all so close a similarity in their percentage composition that the results appear rather to indicate that this mineral may be a definite compound.

The analyses of a large number of specimens of nickeliferous pyrrhotine from various localities appear to show the probability of another definite compound containing about 4 per cent. of nickel. This is extremely common, and has been met with by the author in Norway, Sweden, Italy, Germany, and the United States. A combination of 15 ($Fe^7 S^8$) + NiS would by calculation yield—

Sulphur	38·78
Iron	57·12
Nickel	4·10
	100·00

In Greg and Lettsom's 'Mineralogy of Great Britain,' an analysis of the ore from this mine is cited (p. 297), and stated to be an average of the rough ore. The numbers given are—

Iron	43·76
Nickel	14·22
Sulphur	34·46
Silica	5·90
Lime	1·45
	99·79

No other analysis of any British specimen of this mineral appears recorded. Numerous determinations of the percentage of nickel in the ore from this mine, made by the author, never afforded results anything like approaching to the above; even with the most careful picking, and employing only the purest and richest parts in the analysis, the highest percentage of nickel found did not in any case materially exceed 11 per cent. The specimens analyzed were obtained from His Grace the Duke of Argyll (the proprietor of the mine) in 1851; and subsequently others were taken by the author out of the lode, on the occasion of two visits to the mine in 1853 and 1855; the precise specimen the analysis and description of which is here brought forward was obtained in 1855. An average quantity of the ore sampled in 1851 afforded—

Sulphur . . . . 34·21
Iron | . . . . . 44·60
Nickel . . . . .   5·24
Copper . . . .   1·32
Rock-matter . . . 14·63
                  ———
                  100·00

The rock-matter (14·63 per cent. in all) contained a consider-able amount of quartz, along with no less than 5·2 per cent. mag-nesia in combination, but only a trace of lime.

Iron Pyrites.—In the sulphide of iron and nickel obtained from this mine it is very usual to perceive that the bronze colour of the mineral is blotched or studded over with brass-yellow spots more or less round, and varying in diameter from one-sixteenth up to even occasionally half an inch across; the colour and hard-ness of these parts confirmed the supposition that these spots were iron pyrites. It was, however, only when, after the lapse of some years, the pyrrhotine had become quite broken up and dis-aggregated, that it was easy to obtain these portions of the spe-cimens for analysis.

When the pyrrhotine fell to powder by the action of the atmo-sphere these particles were quite unaffected, and were seen to be so many irregular spheres of cupriferous iron pyrites which ex-ternally retained still a sort of skin or crust of pyrrhotine, but, on breaking, at once showed that the mass possessed the bright brass-yellow colour characteristic of pyrites.

Upon making a determination of the specific gravity, it agreed with that of pyrites; for, several of these globules being taken, pulverized, and the magnetic external crust of pyrrhotine removed by a magnet, the mineral was found to possess the specific gra-vity 4·93 at 60° F.

The analysis was conducted in a similar manner to that of the last mineral, excepting only that the copper was precipitated by sulphuretted hydrogen; and the nickel and cobalt present were separated from one another by treating the mixed oxides obtained in the course of the analysis by Plattner's process before the blowpipe.

15·55 grs. yielded 0·01 gr. insoluble quartz, 0·03 gr. free sul-phur, 7·64 grs. sulphate of barytes, 0·64 gr. oxides of nickel and cobalt, 0·23 gr. oxide of copper, and 10·16 grs. sesquioxide of iron. Reducing these data to percentages, we have the com-position as follows :—

Sulphur	49·32
Iron	45·73
Nickel	1·99
Cobalt	1·24
Copper	1·18
Insoluble	0·06
	99·52

A comparison of the results of this analysis of the globules of iron pyrites with those of the nickeliferous pyrrhotine in which they occur imbedded is very interesting. They contain nearly the whole of the cobalt and copper present in the ore, along with a little of the nickel, and would appear to have segregated out of the general mass, carrying with them the copper and cobalt. In the case of the Craigmuir nickeliferous pyrrhotine, where these segregations do not occur, the cobalt is found still remaining with the nickel in the ore.

A curious metallurgical incident may tend to throw some light on this subject. Some years back, at a smelting-works in Norway engaged in producing nickel regulus (a sulphide of iron and nickel with a little copper), a considerable quantity of the regulus broke through the clay bottom of a furnace and remained in a thick sheet of, say, some six inches in depth interbedded between the foundation and the bottom of the furnace; at the same time, whilst it was protected from oxidation by the latter, it had no doubt remained some months at a temperature much below fusion, and probably had been at no time higher than a red heat. Upon breaking up the bottom to reline the furnace, it was found that this mass of regulus had undergone a very remarkable change; for instead of being a homogeneous and uniform mass of one character as originally, it had now in great part been converted into a mass of small round spherical concretions, varying in diameter from $\frac{1}{16}$ to $\frac{1}{2}$ an inch, almost resembling an oolitic limestone in structure, and which had evidently been formed by a species of segregation or molecular movement in the solid mass of regulus. A chemical examination has not as yet been made, but is likely to afford interesting results.

The segregation of these spherules of sulphide of iron seems to have carried the cobalt contained in the mineral along with them; for it was only with some difficulty that a trace of cobalt could be detected in the pyrrhotine in which they were imbedded; and it is curious that there appears to be a tendency for cobalt to associate itself with the bisulphide of iron (pyrites), whilst nickel appears to prefer uniting itself with the magnetic sulphide (pyrrhotine).

A chemical examination of several hundred specimens of iron

pyrites and magnetic pyrites taken from mineral lodes and erup-
tive rocks, proved that nickel was very rarely found in iron
pyrites (Fe S^2) when not accompanied by pyrrhotine, but that
cobalt was very commonly present in small quantity,—and, on
the other hand, that cobalt was equally seldom in magnetic py-
rites (Fe^7 S^8) if unaccompanied by iron pyrites,—also that when
both these metals were present in a specimen of pyrites, the
nickel greatly preponderated when the pyrites in question was
magnetic (pyrrhotine), whilst the reverse was found to be the
case when it was the bisulphide of iron or ordinary so-called iron
pyrites.

Sulphide of Iron and Nickel from the Craigmuir mine on the
side of Loch Fyne, about eight miles below Inverary, the lode
traversing metamorphic strata, and disturbed by intersecting trap-
pean dykes.—The specific gravity of the pure mineral was found to
be 4·602 at 60° F. The general characters of the mineral corre-
sponded very closely with those of the specimen from Inverary,
the colour alone differing in having a somewhat more dark-bronze
tint, probably due to the entire absence of iron pyrites in the
specimen submitted to examination. The blowpipe reactions
were quite identical with those of the Inverary mineral, and the
chemical analysis was conducted in precisely the same manner.
The results of the analysis of a specimen (as pure as possible)
taken out of the lode in April 1855 was as follows :—Mineral
employed 34·15 grs., which yielded 0·13 gr., or 0·38 per cent.
insoluble matter, consisting entirely of quartz with a few flakes
of silvery mica ; 0·03 gr. free sulphur ; 94·26 grs. sulphate of
barytes ; 24·04 grs. sesquioxide of iron, from which 0·02 gr.
arsenic acid was subsequently separated by precipitation with
sulphuretted hydrogen in the state of sulphide. Another por-
tion, 20·03 grs. in weight, was employed for the determination
of the nickel and cobalt, and yielded 2·81 grs. of the mixed
oxides, in which the cobalt was determined by Plattner's method.
These data make the chemical composition, when tabulated, ap-
pear as follows :—

Sulphur	37·99
Iron	50·87
Nickel	10·01
Cobalt	1·02
Copper	traces
Arsenic	0·04
Silica and mica . .	0·38
	100·31

The results correspond closely with those obtained when the

Inverary mineral was examined; and although several other specimens of the purest mineral obtainable were assayed for nickel, none of them yielded a higher percentage of that mineral than the above.

Gersdorffite.

Locality: Craigmuir nickel mine on the side of Loch Fyne, eight miles below Inverary, Argyleshire, where it was found by the author in April 1855, occurring in a small string or crosscourse intersecting the main lode of sulphide of iron and nickel. This mineral does not appear to have been previously observed as a British species, and is not noticed in Greg and Lettsom's 'Mineralogy of Great Britain.' It is not improbable, however, that the smaltine which, in page 302 of that work, is stated to occur in "Argyleshire, at Essochossan Glen, two miles from Inverary, dispersed in small bright patches in Eisennickelkies," may in reality prove to be this mineral.

The specimen here described was broken out, in the deepest part of the mine, from a small string of nearly pure Gersdorffite, about from 1 to 2 inches wide. It was a compact aggregate of minute indistinct crystals along with quartz and a talcose mineral. In places patches and strings of copper pyrites were visible; but little or no sulphide of iron and nickel occurred with it, notwithstanding that this last-mentioned mineral formed the mass of the main lode, and the object of the explorations. The Gersdorffite had not as yet attracted the attention of the miners.

By pulverizing the ore and washing in a batea, it was found quite easy to obtain the Gersdorffite in a nearly pure state, in the shape of irregular crystalline grains and fragmentary crystals, which, however, were not sufficiently perfect to enable its crystalline form to be settled with certainty, although it appeared to be monometric.

The characters of this mineral are as follows:—crystallized; opake; lustre metallic; colour white to greyish white, tarnishing to a greyish-brown tinge; streak black; powder blackish grey; fracture granular; brittle; hardness 3·75, rather below fluorspar: the specific gravity, taken on two different specimens of the crystalline grains previously washed as free as possible from adherent quartz, was found to be respectively 5·65 and 5·49 at 60° F.

Heated in a closed tube the mineral decrepitates and gives off a considerable sublimate of reddish-yellow sulphide of arsenic, which is transparent both whilst hot and cold. In an open tube it yields a similar sublimate, along with a white one of arsenious acid, and evolves sulphurous acid. Heated with soda on charcoal, the residue reacts strongly for sulphur when placed upon

silver, or when tested with nitroprusside of sodium. When cal-
cined on charcoal and then treated with borate, it shows the re-
actions of nickel and iron,—the former reaction so strong, how-
ever, as generally to obscure the reactions both of the iron and
cobalt which it contains. The iron-reaction is evident, however,
by treating the raw mineral for only a very short time with borate
in the oxidating-flame. The cobalt-reaction is easily obtained
by fusing a portion of the calcined mineral on charcoal with bo-
rate in the reducing-flame of the blowpipe and adding a small
globule of gold, which, by uniting with the reduced nickel, re-
moves it from the glass and allows the cobalt-colour to show
itself distinctly.

The qualitative examination showed the mineral to contain
arsenic, sulphur, nickel, and iron in large amount, along with a
smaller quantity of cobalt and manganese, as also some silica and
insoluble rock-matter from which a little magnesia had been re-
moved by the action of the acid. Traces only of copper were
found present.

The quantitative analysis was conducted as follows :—

I. A weighed portion of the mineral in fine powder was well
mixed with six times its weight of a mixture of equal parts of
pure nitrate of potash and carbonate of soda, and fused in a
porcelain crucible ; the resulting mass was boiled with hot water
repeatedly and filtered. This filtrate was acidified with hydro-
chloric acid, and then neutralized with ammonia in order to see
whether any substance precipitable by ammonia was contained in
the solution ; but as this was found not to be the case, the whole
was again acidified by hydrochloric acid, and a solution (in nitric
acid) of 12·46 grains of iron wire of known purity added to it,
after which the whole was precipitated by ammonia and deter-
mined as usual : the weight of the precipitate, less the amount of
sesquioxide of iron from the quantity of iron added, gave the
amount of arsenic acid equivalent to the arsenic in the mineral.

From the filtrate, after being rendered slightly acid with hy-
drochloric acid, the sulphur was estimated by precipitation as
sulphate of baryta after adding chloride of barium in excess.
The iron was determined in the oxides remaining upon the filter
after having treated the fused residue with water; this was dis-
solved in hydrochloric acid, treated in the cold with carbonate of
barytes, and the precipitate containing the iron was dissolved in
sulphuric acid, filtered from the sulphate of barytes, and the ses-
quioxide of iron in the solution precipitated by ammonia and de-
termined as usual. An unfortunate accident prevented the other
substances being determined in the filtrate from the iron preci-
pitate. In order, therefore, to determine the nickel, cobalt, man-
ganese, and magnesia, another portion was taken and dissolved

in nitrohydrochloric acid, a quantity of iron added and dissolved in the solution, which then was precipitated in the cold by carbonate of barytes; after filtration the excess of baryta was removed from the solution by the addition of sulphuric acid. The filtrate was then precipitated by colourless sulphide of ammonia, and the manganese separated from the sulphides of nickel and cobalt by acetic acid, and, after precipitation from the acid solution by sulphide of ammonium, was determined as usual. After boiling the filtrate and separating some free sulphur by filtration, the magnesia was precipitated as ammoniacal magnesian phosphate and determined as pyrophosphate of magnesia. The sulphides of nickel and cobalt were dissolved in nitrohydrochloric acid and precipitated as oxides by caustic potash; the amount of cobalt in the same was then determined by Plattner's method.

II. For the sake of confirming the results, a second analysis was made by a different method, namely :—A weighed portion was dissolved in nitrohydrochloric acid ; a small amount of silica and free sulphur remained undissolved, which were determined, and afterwards the amount of free sulphur determined as ignition loss. To the filtrate was added chloride of barium in order to throw down the sulphuric acid, which was then determined as sulphate of baryta. The excess of baryta was now removed from the solution by adding sulphuric acid and filtering; the solution was treated with a current of sulphuretted hydrogen passed through it for several hours, during which it was kept on a warm sand-bath; it was then allowed to stand some eight hours, and, after again passing a current of hydrogen through it, was filtered, and the sulphide of arsenic oxidized by nitrohydrochloric acid, filtered from free sulphur, and, after adding the solution of a weighed amount of iron, was precipitated by ammonia. The other constituents were determined as usual, except that the separation of the iron from the nickel and cobalt was effected by treating the sulphides with weak hydrochloric acid. The amounts employed and obtained in these two analyses were as follows :—

I. 18·29 grs. mineral employed; 12·46 grs. iron wire; sulphate of baryta obtained, 26·78 grs., equal to 3·67 sulphur, or 20·01 per cent.; 27·50 grs. sesquioxide of iron with arsenic acid; and this, less 17·84 grs. sesquioxide of iron, left 9·66 grs. arsenic acid, equivalent to 6·30 metallic arsenic, or 34·45 per cent. 20·04 grs. mineral afforded oxides of nickel and cobalt 7·11 grs., protoperoxide of manganese 0·098 gr., pyrophosphate of magnesia 0·37 gr.

II. 20·01 grs. mineral gave 0·17 silica, 0·68 free sulphur, 22·81 sulphate of barytes, 55·19 sesquioxide of iron with arsenic acid, less 44·19 sesquioxide of iron from iron wire, sesquioxide of iron 3·16 grs.

The results tabulated give the following percentage composition :—

	I.	II.
Arsenic	34·45	35·84
Sulphur	20·01	19·75
Nickel	21·59	23·16
Cobalt	6·32	6·64
Iron	13·12	11·02
Manganese	0·33	0·33
Copper	trace	traces
Magnesia	0·66	0·66
Insoluble silica, &c. .	2·71	2·60
	99·19	100·00

The analyses on record of this mineral species from different localities vary greatly in percentage composition, although they are all considered to come under the general formula $Ni (S As)^2$. The above analysis does not differ more from those generally cited than they do from one another, the only remarkable features being that the percentage of arsenic is somewhat lower than usual.

In composition it appears to resemble somewhat the crystallized specimens from Schladming in Styria, which also contain considerably less arsenic than the formula would require.

XXI. *An Experiment in Magneto-Electric Induction.* By W. R. GROVE, *F.R.S. &c.*[*]

SHORTLY after the publication of Mr. Wilde's experiments on magneto-electric induction, it occurred to me that some of the ordinary effects of the Ruhmkorff-coil might be produced by applying to it a magneto-electric machine. I tried an ordinary medical machine with a small coil made by Mr. Apps, of $3\frac{1}{2}$ inches length by 2 inches diameter, and having about $\frac{3}{4}$ of a mile of fine secondary wire.

The result was very unexpected. The terminals of the magneto-electric coils being connected with the primary coil of the Ruhmkorff, and the contact-breaker being kept closed so as to make a completed circuit of the primary wire (a condition which would have appeared *à priori* essential to success), no effect was produced; while if the circuit was interrupted by keeping the contact-breaker open, sparks of 0·3 of an inch passed between the terminals of the secondary coil of the Ruhmkorff, and vacuum-tubes were readily illuminated. Here there was in effect no pri-

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[*] Communicated by the Author.

mary coil, no metallic connexion for the primary current; and yet a notable effect was produced.

I did not at the time publish this experiment further than by communicating it to a few friends, hoping to be able to find a satisfactory explanation of it. All I have observed since is that the effect is dependent upon the condenser; for when that is removed no result is produced.

It would appear, then, to depend on an electrical wave or impulse shot, so to speak, into the uncompleted primary coil, similar to the wave which will deflect in succession magnetic needles placed at different distances on a telegraphic cable, without the current passing through the whole length of wire, as shown in the experiments of Mr. Latimer Clark and others. But why there should be no effect, or an inappreciable one, when the primary circuit is completed, the current being alternated by the rotation of the coils of the magneto-electric machine, I cannot satisfactorily explain.

XXII. *On the Dynamical Theory of Gases.* By J. Clerk Maxwell, *F.R.SS.L. & E.*

[Concluded from p. 145.]

On the Final Distribution of Velocity among the Molecules of Two Systems acting on one another according to any Law of Force.

FROM a given point O let lines be drawn representing in direction and magnitude the velocities of every molecule of either kind in unit of volume. The extremities of these lines will be distributed over space in such a way that if an element of volume dV be taken anywhere, the number of such lines which will terminate within dV will be $f(r)d$V, where r is the distance of dV from O.
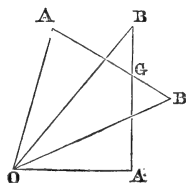
Let OA $= a$ be the velocity of a molecule of the first kind, and OB $= b$ that of a molecule of the second kind before they encounter one another, then BA will be the velocity of A relative to B; and if we divide AB in G inversely as the masses of the molecules, and join OG, OG will be the velocity of the centre of gravity of the two molecules.

Now let OA$' = a'$ and OB $= b'$ be the velocities of the two molecules after the encounter, GA $=$ GA$'$ and GB $=$ GB$'$, and A$'$GB$'$ is a straight line not necessarily in the plane of OAB. Also AGA$' = 2\theta$ is the angle through which the relative velocity is turned in the encounter in question. The relative motion of

the molecules is completely defined if we know $\mathbf{BA}$ the relative velocity before the encounter, 2θ the angle through which $\mathbf{BA}$ is turned during the encounter, and ϕ the angle which defines the direction of the plane in which $\mathbf{BA}$ and $\mathbf{B'A'}$ lie. All encounters in which the magnitude and direction of $\mathbf{BA}$, and also θ and ϕ, lie within certain almost contiguous limits, we shall class as encounters of the given kind. The number of such encounters in unit of time will be

$$n_1 \dot{n}_2 \mathrm{F} de, \qquad \ldots \ldots \ldots \quad (17)$$

where n_1 and n_2 are the numbers of molecules of each kind under consideration, and F is a function of the relative velocity and of the angle θ, and de depends on the limits of variation within which we class encounters as of the same kind.

Now let A describe the boundary of an element of volume $d\mathrm{V}$ while AB and A'B' move parallel to themselves, then B, A', and B' will also describe equal and similar elements of volume.

The number of molecules of the first kind, the lines representing the velocities of which terminate in the element $d\mathrm{V}$ at A, will be

$$n_1 = f_1(a) d\mathrm{V}. \qquad \ldots \ldots \ldots \quad (18)$$

The number of molecules of the second kind which have velocities corresponding to OB will be

$$n_2 = f_2(b) d\mathrm{V}; \qquad \ldots \ldots \ldots \quad (19)$$

and the number of encounters of the given kind between these two sets of molecules will be

$$f_1(a) f_2(b) d\mathrm{V}^2 \mathrm{F} de. \qquad \ldots \ldots \ldots \quad (20)$$

The lines representing the velocities of these molecules after encounters of the given kind will terminate within elements of volume at A' and B', each equal to $d\mathrm{V}$.

In like manner we should find for the number of encounters between molecules whose original velocities corresponded to elements equal to $d\mathrm{V}$ described about A' and B', and whose subsequent velocities correspond to elements equal to $d\mathrm{V}$ described about A and B,

$$f_1(a') f_2(b') d\mathrm{V}^2 \mathrm{F}' de, \qquad \ldots \ldots \ldots \quad (21)$$

where F' is the same function of B'A' and A'GA that F is of BA and AGA'. F is therefore equal to F'.

When the number of pairs of molecules which change their velocities from OA, OB to OA' OB' is equal to the number which change from OA', OB' to OA, OB, then the final distribution of velocity will be obtained, which will not be altered by

subsequent exchanges. This will be the case when

$$f_1(a)f_2(b) = f_1(a')f_2(b'). \quad \cdots \quad \cdots \quad (22)$$

Now the only relation between a, b and a', b' is

$$M_1a^2 + M_2b^2 = M_1a'^2 + M_2b'^2, \quad \cdots \quad (23)$$

whence we obtain

$$f_1(a) = C_1 e^{-\frac{a^2}{a^2}}, \quad f_2(b) = C_2 e^{-\frac{b^2}{\beta^2}}, \quad \cdots \quad (24)$$

where

$$M_1\alpha^2 = N_2\beta^2. \quad \cdots \quad \cdots \quad \cdots \quad (25)$$

By integrating $\iiint C_1 e^{-\frac{\xi^2+\eta^2}{a^2}} \, d\xi \, d\eta \, d\zeta$, and equating the result to N_1, we obtain the value of C_1. If, therefore, the distribution of velocities among N_1 molecules is such that the number of molecules whose component velocities are between ξ and $\xi + d\zeta$, η and $\eta + d\eta$, and ζ and $\zeta + d\zeta$ is

$$dN_1 = \frac{N_1}{\alpha^3 \pi^{\frac{3}{2}}} \, e^{-\frac{\xi^2+\eta^2+\zeta^2}{a^2}} \, d\xi \, d\eta \, d\zeta, \quad \cdots \quad (26)$$

then this distribution of velocities will not be altered by the exchange of velocities among the molecules by their mutual action.

This is therefore a possible form of the final distribution of velocities. It is also the only form; for if there were any other, the exchange between velocities represented by OA and OA' would not be equal. Suppose that the number of molecules having velocity OA' increases at the expense of OA. Then, since the total number of molecules corresponding to OA' remains constant, OA' must communicate as many to OA'', and so on till they return to OA.

Hence, if OA, OA', OA'', &c. be a series of velocities, there will be a tendency of each molecule to assume the velocities OA, OA', OA'', &c. in order, returning to OA. Now it is impossible to assign a reason why the successive velocities of a molecule should be arranged in this cycle, rather than in the reverse order. If, therefore, the direct exchange between OA and OA' is not equal, the equality cannot be preserved by exchange in a cycle. Hence the direct exchange between OA and OA' is equal, and the distribution we have determined is the only one possible.

This final distribution of velocity is attained only when the molecules have had a great number of encounters; but the great rapidity with which the encounters succeed each other is such that in all motions and changes of the gaseous system except the most violent, the form of the distribution of velocity is only slightly changed.

When the gas moves in mass, the velocities now determined are compounded with the motion of translation of the gas.

When the differential elements of the gas are changing their figure, being compressed or extended along certain axes, the values of the mean square of the velocity will be different in different directions. It is probable that the form of the function will then be

$$f_1(\xi\eta\zeta) = \frac{N_1}{\alpha\beta\gamma\pi^{\frac{3}{2}}} \, e^{-\left(\frac{\xi^2}{\alpha^2} + \frac{\eta^2}{\beta^2} + \frac{\zeta^2}{\gamma^2}\right)}, \quad . \quad . \quad . \quad (27)$$

where α, β, γ are slightly different. I have not, however, attempted to investigate the exact distribution of velocities in this case, as the theory of motion of gases does not require it.

When one gas is diffusing through another, or when heat is being conducted through a gas, the distribution of velocities will be different in the positive and negative directions, instead of being symmetrical, as in the case we have considered. The want of symmetry, however, may be treated as very small in most actual cases.

The principal conclusions which we may draw from this investigation are as follows, calling α the modulus of velocity :—

1st. The mean velocity is

$$\bar{v} = \frac{2}{\sqrt{\pi}}\alpha. \quad . \quad . \quad . \quad . \quad . \quad (28)$$

2nd. The mean square of the velocity is

$$\overline{v^2} = \tfrac{3}{2}\alpha^2. \quad . \quad . \quad . \quad . \quad . \quad (29)$$

3rd. The mean value of ξ^2 is

$$\overline{\xi^2} = \tfrac{1}{2}\alpha^2. \quad . \quad . \quad . \quad . \quad . \quad (30)$$

4th. The mean value of ξ^4 is

$$\overline{\xi^4} = \tfrac{3}{4}\alpha^4. \quad . \quad . \quad . \quad . \quad . \quad (31)$$

5th. The mean value of $\xi^2\eta^2$ is

$$\overline{\xi^2\eta^2} = \tfrac{1}{4}\alpha^4. \quad . \quad . \quad . \quad . \quad . \quad (32)$$

6th. When there are two systems of molecules,

$$M_1\alpha^2 = M_2\beta^2, \quad . \quad . \quad . \quad . \quad . \quad (33)$$

whence

$$M_1v_1{}^2 = M_2v_2{}^2, \quad . \quad . \quad . \quad . \quad (34)$$

or the mean *vis viva* of a molecule will be the same in each system. This is a very important result in the theory of gases, and it is independent of the nature of the action between the

molecules, as are all the other results relating to the final distribution of velocities. We shall find that it leads to the law of gases known as that of Equivalent Volumes.

Variation of Functions of the Velocity due to encounters between the Molecules.

We may now proceed to write down the values of $\dfrac{\delta \overline{Q}}{\delta t}$ in the different cases. We shall indicate the mean value of any quantity for all the molecules of one kind by placing a bar over the symbol which represents that quantity for any particular molecule; but in expressions where all such quantities are to be taken at their mean values, we shall, for convenience, omit the bar. We shall use the symbols δ_1 and δ_2 to indicate the effect produced by molecules of the first kind and second kind respectively, and δ_3 to indicate the effect of external forces. We shall also confine ourselves to the case in which $n=5$, since it is not only free from mathematical difficulty, but is the only case which is consistent with the laws of viscosity of gases.

In this case V disappears, and we have for the effect of the second system or the first,

$$\frac{\delta Q}{\delta t} = N_2 \left(\frac{K(M_1 + M_2)}{M_1 M_2} \right)^{\frac{1}{2}} A \int_0^{2\pi} (Q' - Q) d\phi, \quad . \quad (35)$$

where the functions of ζ, η, ζ in $\int (Q' - Q) d\phi$ must be put equal to their mean values for all the molecules, and A_1 or A_2 must be put for A according as $\sin^2 \theta$ or $\sin^2 2\theta$ occurs in the expressions in equations (4), (5), (6), (7). We thus obtain:—

(α) $$\frac{\delta_2 \xi_1}{\delta t} = \left(\frac{K}{M_1 M_2 (M_1 + M_2)} \right)^{\frac{1}{2}} N_2 M_2 A_1 (\xi_2 - \xi_1); \quad . \quad . \quad (36)$$

(β) $$\frac{\delta_2 \xi_1{}^2}{\delta t} = \left(\frac{K}{M_1 M_2 (M_1 + M_2)} \right)^{\frac{1}{2}} \frac{N_2 M_2}{M_1 + M_2}$$
$$\left. \{ 2 A_1 (\xi_2 - \xi_1)(M_1 \xi_1 + M_2 \xi_2) + A_2 M_2 \overline{(\eta_2 - \eta_1}^2 + \overline{\zeta_2 - \zeta_1}^2} \right.$$
$$\left. - 2 \overline{\xi_2 - \xi_1}^2) ; \right\} \quad (37)$$

$$\frac{\delta_2 \xi_1 \eta_1}{\delta t} = \left(\frac{K}{M_1 M_2 (M_1 + M_2)} \right)^{\frac{1}{2}} \frac{N_3 M_2}{M_1 + M_2}$$
$$\left. \{ A_1 \big(2 M_2 \xi_2 \eta_2 - 2 M_1 \xi_1 \eta_1 + (M_1 - M_2)(\xi_1 \eta_2 + \xi_2 \eta_1) \big) \right.$$
$$\left. - 3 A_2 M_2 (\xi_2 - \xi_1)(\eta_2 - \eta_1) \} ; \right\} \quad (38)$$

$(\gamma) \quad \dfrac{\delta_2 \xi_1 V_1}{\delta t}$

$$
\left. \begin{aligned}
= & \left(\frac{K}{M_1 M_2 (M_1 + M_2)}\right)^{\frac{1}{2}} N_2 M_2 \Big\{ A_1 \big(\overline{\xi_2 - \xi_1} V_1{}^2 + 2\xi_1 (U - V_1{}^2)\big) \\
& + \frac{M_2}{M_1 + M_2} (2A_1 - 3A_2) 2 (\xi_2 - \xi_1)(U - V_1{}^2) \\
& + \frac{M_2}{M_1 + M_2} (2A_1 + 2A_2) \xi_1 V^2 \\
& + \left(\frac{M_2}{M_1 + M_2}\right)^2 (2A_1 - 2A_2) 2 (\xi_2 - \xi_1) V^2 \Big\} \ ;
\end{aligned} \right\} \quad (39)
$$

using the symbol δ_2 to indicate variations arising from the action of molecules of the second system.

These are the values of the rate of variation of the mean values of ξ_1, $\xi_1{}^2 \xi_1 \eta_1$, and $\xi_1 V_1{}^2$, for the molecules of the first kind due to their encounters with molecules of the second kind. In all of them we must multiply up all functions of ξ, η, ζ, and take the mean values of the products so found. As this has to be done for all such functions, I have omitted the bar over each function in these expressions.

To find the rate of variation due to the encounters among the particles of the same system, we have only to alter the suffix $_{(2)}$ into $_{(1)}$ throughout, and to change K, the coefficient of the force between M_1 and M_2 into K_1, that of the force between two molecules of the first system. We thus find :—

$(\alpha) \quad \dfrac{\delta_1 \overline{\xi_1}}{\delta t} = 0 ; \quad \cdots \cdots \cdots \cdots \cdots \quad (40)$

$(\beta) \quad \dfrac{\delta_1 \overline{\xi_1{}^2}}{dt} = \left(\dfrac{K_1}{2M_1{}^3}\right)^{\frac{1}{2}} M_1 N_1 A_2 \left\{ \overline{\eta_1{}^2} + \overline{\zeta_1{}^2} - 2\overline{\xi_1{}^2} \right.$

$\left. \qquad\qquad - (\overline{\eta_1 \cdot \eta_1} + \overline{\zeta_1 \cdot \zeta_1} - 2\xi_1 \overline{\xi_1}) \right\} ; \Bigg\} \quad (41)$

$\dfrac{\delta_1 \overline{\xi_1 \eta_1}}{\delta t} = \left(\dfrac{K_1}{2M_1{}^3}\right)^{\frac{1}{2}} M_1 N_1 A_2 3 \{ \overline{\xi_1} \cdot \overline{\eta_1} - \overline{\xi_1 \eta_1} \} ; \quad \cdots \quad (42)$

$(\gamma) \quad \dfrac{\delta_1 \overline{\xi_1 V_1{}^2}}{\delta t} = \left(\dfrac{K_1}{2M_1{}^3}\right)^{\frac{1}{2}} M_1 N_1 A_2 3 (\overline{\xi_1} \cdot \overline{V_1{}^2} - \overline{\xi_1 V_1{}^2}). \quad \cdots \quad (43)$

These quantities must be added to those in equations (36) to (39) in order to get the rate of variation in the molecules of the first kind due to their encounters with molecules of both systems. When there is only one kind of molecules, the latter equations give the rates of variation at once.

On the Action of External Forces on a System of Moving Molecules.

We shall suppose the external force to be like the force of gravity, producing equal acceleration on all the molecules. Let the components of the force in the three coordinate directions be X, Y, Z. Then we have by dynamics for the variations of ξ, ξ^2, and ξV^2 due to this cause :—

$$(\alpha) \quad \frac{\delta_3 \xi}{\delta t} = X ; \quad \dots \dots \dots \quad (44)$$

$$(\beta) \quad \frac{\delta_3 \cdot \xi^2}{\delta t} = 2\xi X ; \quad \dots \dots \dots \quad (45)$$

$$\frac{\delta_3 \cdot \xi \eta}{\delta t} = \eta X + \xi Y ; \quad \dots \dots \dots \quad (46)$$

$$(\gamma) \quad \frac{\delta_3 \cdot \xi V^2}{\delta t} = 2\xi(\xi X + \eta Y + \zeta Z) + X V^2 ; \quad \dots \quad (47)$$

where δ_3 refers to variations due to the action of external forces.

On the Total rate of change of the different functions of the velocity of the molecules of the first system arising from their encounters with molecules of both systems and from the action of external forces.

To find the total rate of change arising from these causes, we must add

$$\frac{\delta_1 Q}{\delta t}, \quad \frac{\delta_2 Q}{\delta t}, \quad \text{and} \quad \frac{\delta_3 Q}{\delta t},$$

the quantities already found. We shall find it, however, most convenient in the remainder of this investigation to introduce a change in the notation, and to substitute for

$$\xi, \eta, \text{ and } \zeta, \quad u+\xi, \quad v+\eta, \text{ and } w+\zeta, \quad \dots \quad (48)$$

where u, v, and w are so chosen that they are the mean values of the components of the velocity of all molecules of the same system in the immediate neighbourhood of a given point. We shall also write

$$M_1 N_1 = \rho_1, \quad M_2 N_2 = \rho_2, \quad \dots \dots \quad (49)$$

where ρ_1 and ρ_2 are the densities of the two systems of molecules —that is, the mass in unit of volume. We shall also write

$$\left(\frac{K_1}{2 M_1^3}\right)^{\frac{1}{2}} = k_1, \quad \left(\frac{K}{M_1 M_2 (M_1 + M_2)}\right)^{\frac{1}{2}} = k, \text{ and } \left(\frac{K_2}{2 M_2^3}\right)^{\frac{1}{2}} = k_2 ; \quad (50)$$

ρ_1, ρ_2, k_1, k_2, and k are quantities the absolute values of which can be deduced from experiment. We have not as yet experimental data for determining M, N, or K.

We thus find for the rate of change of the various functions of the velocity :—

$$(\alpha) \qquad \frac{\delta u_1}{\delta t} = k A_1 \rho_2 (u_2 - u_1) + X ; \qquad \dots \dots \qquad (51)$$

$$(\beta) \qquad \frac{\delta . \xi_1^2}{\delta t} = k_1 A_2 \rho_1 \{\eta_1^2 + \zeta_1^2 - 2\xi_1^2\}$$

$$+ k \rho_2 \frac{M_2}{M_1 + M_2} \{2 A_1 (u_2 - u_1)^2 + A_2 (\overline{v_2 - v_1}^2 + \overline{w_2 - w_1}^2 - 2 \overline{u_2 - u_1}^2)\}$$

$$+ \frac{k \rho_2}{M_1 + M_2} \{2 A_1 (M_2 \xi_2^2 - M_1 \xi_1^2) + A_2 M_2 (\eta_1^2 + \zeta_1^2 - 2\xi_1^2 + \eta_2^2$$

$$+ \zeta_2^2 - 2\xi_2^2)\} ; \qquad \dots \dots \dots$$

$$\left.\right\} \ (52)$$

also

$$\frac{\delta . \xi \eta}{\delta t} = -3 k_1 A_2 \rho_1 \xi_1 \eta_1 + k \rho_2 \frac{M_2}{M_1 + M_2} (2 A_1 - 3 A_2)(u_2 - u_1)(v_2 - v_1)$$

$$+ \frac{k \rho_2}{M_1 + M_2} \{2 A_1 (M_2 \xi_2 \eta_2 - M_1 \xi_1 \eta_1) - 3 A_2 M_2 (\xi_1 \eta_1 + \xi_2 \eta_2)\} .$$

$$\left.\right\} \ (53)$$

(γ) As the expressions for the variation of functions of three dimensions in mixed media are complicated, and as we shall not have occasion to use them, I shall give the case of a single medium,

$$\frac{\delta}{\delta t} (\xi_1^3 + \xi_1 \eta_1^2 + \xi_1 \zeta_1^2) = -3 k_1 \rho_1 A_2 (\xi_1^3 + \xi_1 \eta_1^2 + \xi_1 \zeta_1)^2$$

$$+ X(3\xi_1^2 + \eta_1^2 + \zeta_1^2) + 2 Y \xi_1 \eta_1 + 2 Z \xi_1 \zeta_1 .$$

$$\left.\right\} \quad . \quad (54)$$

Theory of a Medium composed of Moving Molecules.

We shall suppose the position of every moving molecule referred to three rectangular axes, and that the component velocities of any one of them, resolved in the directions of x, y, z, are

$$u + \xi, \quad v + \eta, \quad w + \zeta,$$

where u, v, w are the components of the mean velocity of all the molecules which are at a given instant in a given element of volume, and ξ, η, ζ are the components of the relative velocity of one of these molecules with respect to the mean velocity.

The quantities u, v, w may be treated as functions of x, y, z,

and t, in which case differentiation will be expressed by the symbol d. The quantities ξ, η, ζ being different for every molecule, must be regarded as functions of t for each molecule. Their variation with respect to t will be indicated by the symbol δ.

The mean values of ξ^2 and other functions of ξ, η, ζ for all the molecules in the element of volume may, however, be treated as functions of x, y, z, and t.

If we consider an element of volume which always moves with the velocities u, v, w, we shall find that it does not always consist of the same molecules, because molecules are continually passing through its boundary. We cannot, therefore, treat it as a mass moving with the velocity u, v, w, as is done in hydrodynamics, but we must consider separately the motion of each molecule. When we have occasion to consider the variation of the properties of this element during its motion as a function of the time, we shall use the symbol ∂.

We shall call the velocities u, v, w the velocities of translation of the medium, and ξ, η, ζ the velocities of agitation of the molecules.

Let the number of molecules in the element $dx\,dy\,dz$ be N $dx\,dy\,dz$, then we may call N the number of molecules in unit of volume. If M is the mass of each molecule, and ρ the density of the element, then

$$\mathrm{MN} = \rho. \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

Transference of Quantities across a Plane Area.

We must next consider the molecules which pass through a given plane of unit area in unit of time, and determine the quantity of matter, of momentum, of heat, &c. which is transferred from the negative to the positive side of this plane in unit of time.

We shall first divide the N molecules in unit of volume into classes according to the value of ξ, η, and ζ for each, and we shall suppose that the number of molecules in unit of volume whose velocity in the direction of x lies between ξ and $\xi + d\xi$, η and $\eta + d\eta$, ζ and $\zeta + d\zeta$ is dN; dN will then be a function of the component velocities, the sum of which being taken for all the molecules will give N, the total number of molecules. The most probable form of this function for a medium in its state of equilibrium is

$$d\mathrm{N} = \frac{\mathrm{N}}{\alpha^3 \pi^{\frac{3}{2}}} e^{-\frac{\xi^2 + \eta^2 + \zeta^2}{\alpha^2}} d\xi\, d\eta\, d\zeta. \quad . \quad . \quad . \quad (56)$$

In the present investigation we do not require to know the form of this function.

Now let us consider a plane of unit area perpendicular to x

moving with a velocity of which the part resolved parallel to x is u'. The velocity of the plane relative to the molecules we have been considering is $u' - (u + \xi)$; and since there are $d\mathrm{N}$ of these molecules in unit of volume, it will overtake

$$\left(u' - (u + \xi) \right) d\mathrm{N}$$

such molecules in unit of time, and the number of such molecules passing from the negative to the positive side of the plane will be

$$(u + \xi - u')d\mathrm{N}.$$

Now let Q be any property belonging to the molecule, such as its mass, momentum, *vis viva*, &c., which it carries with it across the plane, Q being supposed a function of ξ or of ξ, η, and ζ, or to vary in any way from one molecule to another, provided it be the same for the selected molecules whose number is $d\mathrm{N}$, then the quantity of Q transferred across the plane in the positive direction in unit of time is

$$\int (u - u' + \xi) \mathrm{Q} d\mathrm{N},$$

or

$$(u - u')\int \mathrm{Q} d\mathrm{N} + \int \xi \mathrm{Q} d\mathrm{N}. \quad . \quad . \quad . \quad (57)$$

If we put $\overline{\mathrm{Q}}\mathrm{N}$ for $\int \mathrm{Q} d\mathrm{N}$, and $\overline{\xi\mathrm{Q}}\mathrm{N}$ for $\int \xi \mathrm{Q} d\mathrm{N}$, then we may call $\overline{\mathrm{Q}}$ the mean value of Q, and $\overline{\xi\mathrm{Q}}$ the mean value of $\xi\mathrm{Q}$, for all the particles in the element of volume, and we may write the expression for the quantity of Q which crosses the plane in unit of time

$$(u - u')\overline{\mathrm{Q}}\mathrm{N} + \overline{\xi\mathrm{Q}}\mathrm{N}. \quad . \quad . \quad . \quad . \quad (58)$$

(α) *Transference of Matter across a Plane.—Velocity of the Fluid.*

To determine the quantity of matter which crosses the plane, make Q equal to M the mass of each molecule; then, since M is the same for all molecules of the same kind, $\overline{\mathrm{M}} = \mathrm{M}$; and since the mean value of ξ is zero, the expression is reduced to

$$(u - u')\mathrm{MN} = (u - u')\rho. \quad . \quad . \quad . \quad . \quad (59)$$

If $u = u'$, or if the plane moves with velocity u, the whole excess of matter transferred across the plane is zero; the velocity of the fluid may therefore be defined as the velocity whose components are u, v, w.

(β) *Transference of Momentum across a Plane.—System of Pressures at any Point of the Fluid.*

The momentum of any one molecule in the direction of x is

$M(u+\xi)$. Substituting this for Q, we get for the quantity of momentum transferred across the plane in the positive direction

$$(u-u')u\rho + \overline{\xi^2}\rho. \quad \cdots \quad (60)$$

If the plane moves with the velocity u, this expression is reduced to $\overline{\xi^2}\rho$, where $\overline{\xi^2}$ represents the mean value of ξ^2.

This is the whole momentum in the direction of x of the molecules projected from the negative to the positive side of the plane in unit of time. The mechanical action between the parts of the medium on opposite sides of the plane consists partly of the momentum thus transferred, and partly of the direct attractions or repulsions between molecules on opposite sides of the plane. The latter part of the action must be very small in gases; so that we may consider the pressure between the parts of the medium on opposite sides of the plane as entirely due to the constant bombardment kept up between them. There will also be a transference of momentum in the directions of y and z across the same plane,

$$(u-u')v\rho + \overline{\xi\eta}\rho, \quad \cdots \quad (61)$$

and

$$(u-u')w\rho + \overline{\xi\zeta}\rho, \quad \cdots \quad (62)$$

where $\overline{\xi\eta}$ and $\overline{\xi\zeta}$ represent the mean values of these products.

If the plane moves with the mean velocity u of the fluid, the total force exerted on the medium on the positive side by the projection of molecules into it from the negative side will be

a normal pressure $\overline{\xi^2}\rho$ in the direction of x,

a tangential pressure $\overline{\xi\eta}\rho$ in the direction of y,

and a tangential pressure $\overline{\xi\zeta}\rho$ in the direction of z.

If X, Y, Z are the components of the pressure on unit of area of a plane whose direction-cosines are l, m, n,

$$\left.\begin{array}{l} X = l\overline{\xi^2}\rho + m\overline{\xi\eta}\rho + n\overline{\xi\zeta}\rho, \\ Y = l\overline{\xi\eta}\rho + m\overline{\eta^2}\rho + n\overline{\eta\zeta}\rho, \\ Z = l\overline{\xi\zeta}\rho + m\overline{\eta\zeta}\rho + n\overline{\zeta^2}\rho. \end{array}\right\} \quad \cdots \quad (63)$$

When a gas is not in a state of violent motion the pressures in all directions are nearly equal, in which case, if we put

$$\overline{\xi^2}\rho + \overline{\eta^2}\rho + \overline{\zeta^2}\rho = 3p, \quad \cdots \quad (64)$$

the quantity p will represent the mean pressure at a given point, and $\overline{\xi^2}\rho$, $\overline{\eta^2}\rho$, and $\overline{\zeta^2}\rho$ will differ from p only by small quantities; $\overline{\eta\zeta}\rho$, $\overline{\zeta\xi}\rho$, and $\overline{\xi\eta}\rho$ will then be also small quantities with respect to p.

Energy in the Medium.—Actual Heat.

The actual energy of any molecule depends partly on the velocity of its centre of gravity, and partly on its rotation or other internal motion with respect to the centre of gravity. It may be written

$$\tfrac{1}{2}M\left\{(u+\xi)^2+(v+\eta)^2+(w+\zeta)^2\right\}+\tfrac{1}{2}EM, \quad . \quad . \quad (65)$$

where $\tfrac{1}{2}EM$ is the internal part of the energy of the molecule, the form of which is at present unknown. Summing for all the molecules in unit of volume, the energy is

$$\tfrac{1}{2}(u^2+v^2+w^2)\rho+\tfrac{1}{2}(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\rho+\tfrac{1}{2}\overline{E}\rho. \quad . \quad . \quad (66)$$

The first term gives the energy due to the motion of translation of the medium in mass, the second that due to the agitation of the centres of gravity of the molecules, and the third that due to the internal motion of the parts of each molecule.

If we assume, with Clausius, that the ratio of the mean energy of internal motion to that of agitation tends continually towards a definite value $(\beta-1)$, we may conclude that, except in very violent disturbances, this ratio is always preserved, so that

$$\overline{E}=(\beta-1)(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2}). \quad . \quad . \quad . \quad (67)$$

The total energy of the invisible agitation in unit of volume will then be

$$\tfrac{1}{2}\beta(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})\rho, \quad . \quad . \quad . \quad . \quad . \quad (68)$$

or

$$\tfrac{3}{2}\beta p. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (69)$$

This energy, being in the form of invisible agitation, may be called the total heat in the unit of volume of the medium.

(γ) Transference of Energy across a Plane.—Conduction of Heat.

Putting

$$Q=\tfrac{1}{2}\beta(\overline{\xi^2}+\overline{\eta^2}+\overline{\zeta^2})M, \text{ and } u=u', \quad . \quad . \quad (70)$$

we find for the quantity of heat carried over the unit of area by conduction in unit of time

$$\tfrac{1}{2}\beta(\overline{\xi^3}+\overline{\xi\eta^2}+\overline{\xi\zeta^2})\rho, \quad . \quad . \quad . \quad . \quad (71)$$

where ξ^3 &c. indicate the mean values of ξ^3 &c. They are always small quantities.

On the Rate of Variation of Q *in an Element of Volume,* Q *being any property of the Molecules in that Element.*

Let Q be the value of the quantity for any particular molecule, and $\overline{Q}$ the mean value of Q for all the molecules of the same kind within the element.

The quantity $\overline{Q}$ may vary from two causes. The molecules within the element may by their mutual action or by the action of external forces produce an alteration of $\overline{Q}$; or molecules may pass into the element and out of it, and so cause an increase or diminution of the value of $\overline{Q}$ within it. If we employ the symbol δ to denote the variation of Q due to actions of the first kind on the individual molecules, and the symbol ∂ to denote the actual variation of Q in an element moving with the mean velocity of the system of molecules under consideration, then, by the ordinary investigation of the increase or diminution of matter in an element of volume as contained in treatises on Hydrodynamics,

$$\left. \begin{aligned} \frac{\partial \overline{Q}N}{\partial t} = \frac{\delta \overline{Q}}{\delta t}N - \frac{d}{dx}\left\{(u-u')\overline{Q}N + \overline{\xi Q}N\right\} \\ -\frac{d}{dy}\left\{(v-v')\overline{Q}N + \overline{\eta Q}N\right\} - \frac{d}{dz}\left\{(w-w')\overline{Q}N + \overline{\zeta Q}N\right\}, \end{aligned} \right\} (72)$$

where the last three terms are derived from equation (59) and two similar equations, and denote the quantity of Q which flows out of an element of volume, that element moving with the velocities u', v', w'. If we perform the differentiations and then make $u'=u$, $v'=v$, and $w'=w$, then the variation will be that in an element which moves with the actual mean velocity of the system of molecules, and the equation becomes

$$\left. \begin{aligned} \frac{\partial \overline{Q}N}{\partial t} + \overline{Q}N\left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz}\right) + \frac{d}{dx}(\overline{\xi Q}N) + \frac{d}{dy}(\overline{\eta Q}N) \\ + \frac{d}{dz}(\overline{\zeta Q}N) = \frac{\delta Q}{\delta t}N. \quad \ldots \ldots \ldots \end{aligned} \right\} (73)$$

Equation of Continuity.

Put Q=M the mass of a molecule; M is unalterable, and we have, putting MN=ρ,

$$\frac{\partial \rho}{\partial t} + \rho\left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz}\right) = 0, \quad \ldots \quad (74)$$

which is the ordinary equation of continuity in hydrodynamics, the element being supposed to move with the velocity of the

fluid.   Combining this equation with that from which it was obtained, we find

$$N\frac{\partial \overline{Q}}{\partial t} + \frac{d}{dx}(\overline{\xi Q}N) + \frac{d}{dy}(\overline{\eta Q}N) + \frac{d}{dz}(\overline{\zeta Q}N) = N\frac{\delta Q}{\delta t}, \quad (75)$$

a more convenient form of the general equation.

Equations of Motion (α).

To obtain the equation of motion in the direction of x, put $Q = M_1(u_1 + \xi_1)$, the momentum of a molecule in the direction of x.

We obtain the value of $\dfrac{\delta Q}{\delta t}$ from equation (51); and the equation may be written

$$\left. \begin{aligned} \rho_1 \frac{\partial u_1}{\partial t} + \frac{d}{dx}(\rho_1 \overline{\xi_1^2}) + \frac{d}{dy}(\rho_1 \overline{\xi_1 \eta_1}) + \frac{d}{dz}(\rho_1 \overline{\xi_1 \zeta_1}) \\ = k A_1 \rho_1 \rho_2 (u_2 - u_1) + X \rho_1. \quad\quad \end{aligned} \right\} \quad (76)$$

In this equation the first term denotes the efficient force per unit of volume, the second the variation of normal pressure, the third and fourth the variations of tangential pressure, the fifth the resistance due to the molecules of a different system, and the sixth the external force acting on the system.

The investigation of the values of the second, third, and fourth terms must be deferred till we consider the variations of the second degree.

Condition of Equilibrium of a Mixture of Gases.

In a state of equilibrium u_1 and u_2 vanish, $\rho_1 \xi_1^2$ becomes p_1, and the tangential pressures vanish, so that the equation becomes

$$\frac{dp_1}{dx} = X \rho_1, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (77)$$

which is the equation of equilibrium in ordinary hydrostatics.

This equation, being true of the system of molecules forming the first medium independently of the presence of the molecules of the second system, shows that if several kinds of molecules are mixed together, placed in a vessel and acted on by gravity, the final distribution of the molecules of each kind will be the same as if none of the other kinds had been present.   This is the same mode of distribution as that which Dalton considered to exist in a mixed atmosphere in equilibrium, the law of diminution of density of each constituent gas being the same as if no other gases were present.

This result, however, can only take place after the gases have been left for a considerable time perfectly undisturbed.   If cur-

rents arise so as to mix the strata, the composition of the gas will be made more uniform throughout.

The result at which we have arrived as to the final distribution of gases, when left to themselves, is independent of the law of force between the molecules.

Diffusion of Gases.

If the motion of the gases is slow, we may still neglect the tangential pressures. The equation then becomes for the first system of molecules

$$\rho_1 \frac{\partial u_1}{\partial t} + \frac{dp_1}{dx} = k\mathrm{A}_1 \rho_1 \rho_2 (u_2 - u_1) + \mathrm{X}\rho_1, \quad . \quad . \quad (78)$$

and for the second,

$$\rho_2 \frac{\partial u_2}{\partial t} + \frac{dp_2}{dx} = k\mathrm{A}_1 \rho_1 \rho_2 (u_1 - u_2) + \mathrm{X}\rho_2. \quad . \quad . \quad (79)$$

In all cases of quiet diffusion we may neglect the first term of each equation. If we then put $p_1 + p_2 = p$, and $\rho_1 + \rho_2 = \rho$, we find by adding,

$$\frac{dp}{dx} = \mathrm{X}\rho. \quad . \quad . \quad . \quad . \quad . \quad . \quad (80)$$

If we also put $p_1 u_1 + p_2 u_2 = pu$, then the volumes transferred in opposite directions across a plane moving with velocity u will be equal, so that

$$p_1(u_1 - u) = p_2(u - u_2) = \frac{p_1 p_2}{p\rho_1 \rho_2 k\mathrm{A}_1} \cdot \left(\mathrm{X}\rho_1 \frac{dp_1}{dx}\right). \quad . \quad (81)$$

Here $p_1(u_1 - u)$ is the volume of the first gas transferred in unit of time across unit of area of the plane reduced to pressure unity, and at the actual temperature; and $p_2(u - u_2)$ is the equal volume of the second gas transferred across the same area in the opposite direction.

The external force X has very little effect on the quiet diffusion of gases in vessels of moderate size. We may therefore leave it out in our definition of the coefficient of diffusion of two gases.

When two gases not acted on by gravity are placed in different parts of a vessel at equal pressures and temperatures, there will be mechanical equilibrium from the first, and u will always be zero. This will also be approximately true of heavy gases, provided the denser gas is placed below the lighter. Mr. Graham has described, in his paper on the Mobility of Gases*, experiments which were made under these conditions. A ver-

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* Philosophical Transactions, 1863. [Phil. Mag. December 1863.]

tical tube had its lower tenth part filled with a heavy gas, and the remaining nine-tenths with a lighter gas.   After the lapse of a known time the upper tenth part of the tube was shut off, and the gas in it analyzed, so as to determine the quantity of the heavier gas which had ascended into the upper tenth of the tube during the given time.

In this case we have $u = 0$, ... (82)

$$p_1 u_1 = - \frac{p_1 p_2}{\rho_1 \rho_2 k A_1} \frac{1}{p} \frac{dp_1}{dx}, \quad \text{. . . . .} \quad (83)$$

and, by the equation of continuity,

$$\frac{dp_1}{dt} + \frac{d}{dx}(p_1 u_1) = 0, \quad \text{. . . . . .} \quad (84)$$

whence

$$\frac{dp_1}{dt} = \frac{p_1 p_2}{\rho_1 \rho_2 k A_1} \frac{1}{p} \frac{d^2 p_1}{dx^2}; \quad \text{. . . . .} \quad (85)$$

or, if we put $D = \dfrac{p_1 p_2}{\rho_1 \rho_2 k A_1} \dfrac{1}{p}$,

$$\frac{dp_1}{dt} = D \frac{d^2 p_1}{dx^2}. \quad \text{. . . . . . .} \quad (86)$$

The solution of this equation is

$$p_1 = C_1 + C_2 e^{-n^2 D t} \cos(nx + \alpha) + \&c. \quad . \quad (87)$$

If the length of the tube is a, and if it is closed at both ends,

$$p_1 = C_1 + C_2 e^{-\frac{\pi^2 D}{a^2} t} \cos \frac{\pi x}{a} + C_3 e^{-4 \frac{\pi^2 D}{a^2} t} \cos 2 \frac{\pi x}{a} + \&c., \quad (88)$$

where C_1, C_2, C_3 are to be determined by the condition that when $t = 0$, $p_1 = p$, from $x = 0$ to $x = \frac{1}{10} a$, and $p_1 = 0$ from $x = \frac{1}{10} a$ to $x = a$.   The general expression for the case in which the first gas originally extends from $x = 0$ to $x = b$, and in which after a time t the gas from $x = 0$ to $x = c$ is collected, is

$$\frac{p_1}{p} = \frac{b}{a} + \frac{2a}{\pi^2 c} \left\{ e^{-\frac{\pi^2 D}{a^2} t} \sin \frac{\pi b}{a} \sin \frac{\pi c}{a} \right. $$
$$\left. + \frac{1}{2^2} e^{-4 \frac{\pi^2 D}{a^2} t} \sin \frac{2\pi b}{a} \sin \frac{2\pi c}{a} + \&c. \right\}, \quad \right\} \quad \text{. .} \quad (89)$$

where $\dfrac{p_1}{p}$ is the proportion of the first gas to the whole in the portion from $x = 0$ to $x = c$.

In Mr. Graham's experiments, in which one-tenth of the tube

was filled with the first gas, and the proportion of the first gas in the tenth of the tube at the other end ascertained after a time t, this proportion will be

$$\frac{p}{p} = \frac{1}{10} - \frac{20}{\pi^2} \left\{ e^{-\frac{\pi^2 D}{a^2} t} \sin^2 \frac{\pi}{10} - e^{-2^2 \frac{\pi^2 D}{a^2} t} \sin^2 2 \frac{\pi}{10} \right. \\ \left. + e^{-3^2 \frac{\pi^2 D}{a^2} t} \sin^2 3 \frac{\pi}{10} - \&c. \right\}. \quad\quad (90)$$

We find for a series of values of $\frac{p_1}{p}$ taken at equal intervals of time T, where

$$T = \frac{\log_e 10}{10 \pi^2} \frac{a^2}{D}.$$

Time.	$\frac{p_1}{p}$.
0	0
T	·01193
2 T	·02305
3 T	·03376
4 T	·04366
5 T	·05267
6 T	·06072
8 T	·07321
10 T	·08227
12 T	·08845
∞	·10000

Mr. Graham's experiments on carbonic acid and air, when compared with this Table, give $T = 500$ seconds nearly for a tube 0·57 metre long. Now

$$D = \frac{\log_e 10}{10 \pi^2} \frac{a^2}{T}, \quad\quad\quad (91)$$

whence

$$D = ·0235$$

for carbonic acid and air, in inch-grain-second measure.

Definition of the Coefficient of Diffusion.

D is the volume of gas, reduced to unit of pressure, which passes in unit of time through unit of area when the total pressure is uniform and equal to p, and the pressure of either gas increases or diminishes by unity in unit of distance. D may be called the coefficient of diffusion. It varies directly as the square of the absolute temperature, and inversely as the total pressure p.

The dimensions of D are evidently L^2T^{-1}, where L and T are the standards of length and time.

In considering this experiment of the interdiffusion of carbonic acid and air, we have assumed that air is a simple gas. Now it is well known that the constituents of air can be separated by mechanical means, such as passing them through a porous diaphragm, as in Mr. Graham's experiments on Atmolysis. The discussion of the interdiffusion of three or more gases leads to a much more complicated equation than that which we have found for two gases, and it is not easy to deduce the coefficients of interdiffusion of the separate gases. It is therefore to be desired that experiments should be made on the interdiffusion of every pair of the more important pure gases which do not act chemically on each other, the temperature and pressure of the mixture being noted at the time of experiment.

Mr. Graham has also published in Brande's Journal for 1829, pt. 2, p. 74, the results of experiments on the diffusion of various gases out of a vessel through a tube into air. The coefficients of diffusion deduced from these experiments are—

Air and hydrogen . . .	·026216
Air and marsh-gas . . .	·01024
Air and ammonia . . .	·00962
Air and olefiant gas . . .	·00771
Air and carbonic acid . .	·00682
Air and sulphurous acid .	·00582
Air and chlorine	·00486

The value for carbonic acid is only one third of that deduced from the experiment with the vertical column. The inequality of composition of the mixed gas in different parts of the vessel, however, is neglected; and the diameter of the tube at the middle part, where it was bent, was probably less than that given.

Those experiments on diffusion which lasted ten hours, all give smaller values of D than those which lasted four hours; and this would also result from the mixture of the gases in the vessel being imperfect.

Interdiffusion through a small hole.

When two vessels containing different gases are connected by a small hole, the mixture of gases in each vessel will be nearly uniform except near the hole; and the inequality of the pressure of each gas will extend to a distance from the hole depend-

ing on the diameter of the hole, and nearly proportional to that diameter.

Hence in the equation

$$\rho_1 \frac{\partial u_1}{dt} + \frac{dp_1}{dx} = kA\rho_1\rho_2(u_2 - u_1) + X\rho \quad . \quad . \quad (92)$$

the term $\frac{dp_1}{dx}$ will vary inversely as the diameter of the hole, while u_1 and u_2 will not vary considerably with the diameter.

Hence, when the hole is very small, the right-hand side of the equation may be neglected, and the flow of either gas through the hole will be independent of the flow of the other gas, as the term $kA\rho_1\rho_2(u_2 - u_1)$ becomes comparatively insignificant.

One gas, therefore, will escape through a very fine hole into another nearly as fast as into a vacuum; and if the pressures are equal on both sides, the volumes diffused will be as the square roots of the specific gravities inversely, which is the law of diffusion of gases established by Graham*.

Variation of the invisible agitation (β).

By putting for Q in equation (75)

$$\left. Q = \frac{M}{2} \Big((u_1 + \xi_1)^2 + (v_1 + \eta_1)^2 + (w_1 + \zeta_1)^2 \atop + (\beta - 1)(\xi_1^2 + \eta_1^2 + \zeta_1^2) \Big), \right\} \quad . \quad . \quad (93)$$

and eliminating by means of equations (76) and (52), we find

$$\left. \begin{aligned} &\tfrac{1}{2}\rho_1 \frac{\partial}{\partial t}\beta_1(\xi_1^2 + \eta_1^2 + \zeta_1^2) + \rho_1\xi_1^2\frac{du_1}{dx} + \rho_1\eta_1^2\frac{dv_1}{dy} + \rho_1\zeta_1^2\frac{dw_1}{dz} \\ &\quad + \rho_1\eta_1\zeta_1\left(\frac{dv_1}{dz} + \frac{dw_1}{dy}\right) + \rho_1\zeta_1\xi_1\left(\frac{dw_1}{dx} + \frac{du_1}{dz}\right) \\ &\quad + \rho_1\xi_1\eta_1\left(\frac{du_1}{dy} + \frac{dv_1}{dx}\right) + \beta_1\left\{\frac{d}{dx}(\rho_1\xi_1^3 + \rho_1\xi_1\eta_1^2\right. \\ &\quad + \rho_1\xi_1\zeta_1^2) + \frac{d}{dy}(\rho_1\eta_1\xi_1^2 + \rho_1\eta_1^3 + \rho_1\eta_1\zeta_1^2) \\ &\quad + \left. \frac{d}{dz}(\rho_1\zeta_1\xi_1^2 + \rho_1\zeta_1\eta_1^2 + \rho_1\zeta_1^3)\right\} \\ &= \frac{k\rho_1\rho_2 A_1}{M_1 + M_2}\Big\{ M_2[(u_2 - u_1)^2 + (v_2 - v_1)^2 + \overline{(w_2 - w_1)}^2] \\ &\quad + M_2(\xi_2^2 + \eta_2^2 + \zeta_2^2) - M_1(\xi_1^2 + \eta_1^2 + \zeta_1^2)\Big\}. \end{aligned} \right\} \quad (94)$$

In this equation the first term represents the variation of invi-

* Transactions of the Royal Society of Edinburgh, vol. xii. p. 222.

sible agitation or heat; the second, third, and fourth represent the cooling by expansion; the fifth, sixth, and seventh the heating effect of fluid-friction or viscosity; and the last the loss of heat by conduction. The quantities on the other side of the equation represent the thermal effects of diffusion, and the communication of heat from one gas to the other.

The equation may be simplified in various cases, which we shall take in order.

1st. *Equilibrium of Temperature between two Gases.—Law of Equivalent Volumes.*

We shall suppose that there is no motion of translation, and no transfer of heat by conduction through either gas. The equation (94) is then reduced to the following form,

$$\tfrac{1}{2}\rho_1\frac{\partial}{\partial t}\beta_1(\xi_1^2+\eta_1^2+\zeta_1^2)=\frac{k\rho_1\rho_2A_1}{M_1+M_2}\left\{M_2(\xi_2^2+\eta_2^2+\zeta_2^2)-M_1(\xi_1^2+\eta_1^2+\zeta_1^2)\right\}. \quad\quad (95)$$

If we put

$$\left.\begin{array}{l}\dfrac{M_1}{M_1+M_2}(\xi_1^2+\eta_1^2+\zeta_1^2)=Q_1, \quad\text{and}\\[2mm]\dfrac{M_2}{M_1+M_2}(\xi_2^2+\eta_2^2+\zeta_2^2)=Q_2,\end{array}\right\} \quad\quad (96)$$

we find

$$\frac{\partial}{\partial t}(Q_2-Q_1)=-\frac{2kA_1}{M_1+M_2}(M_2\rho_2\beta_1+M_1\rho_1\beta_2)(Q_2-Q_1), \quad (97)$$

or

$$\left.\begin{array}{l}Q_2-Q_1=Ce^{-nt},\\[2mm]\text{where } n=\dfrac{2kA_1}{M_1+M_2}(M_2\rho_2\beta_2+M_1\rho_1\beta_1)\dfrac{1}{\beta_1\beta_2}.\end{array}\right\} \quad (98)$$

If, therefore, the gases are in contact and undisturbed, Q_1 and Q_2 will rapidly become equal. Now the state into which two bodies come by exchange of invisible agitation is called equilibrium of heat or equality of temperature. Hence, when two gases are at the same temperature,

$$Q_1=Q_2, \quad\quad\cdots\cdots\quad (99)$$

or

$$1=\frac{Q_1}{Q_2}=\frac{M_1(\xi_1^2+\eta_1^2+\zeta_1^2)}{M_2(\xi_2^2+\eta_2^2+\zeta_2^2)}$$

$$=\frac{M_1\dfrac{p_1}{\rho_1}}{M_2\dfrac{p_2}{\rho_2}}.$$

Hence if the pressures as well as the temperatures be the same in two gases,

$$\frac{M_1}{\rho_1} = \frac{M_2}{\rho_2}, \qquad \dots \dots \quad (100)$$

or the masses of the individual molecules are proportional to the density of the gas.

This result, by which the relative masses of the molecules can be deduced from the relative densities of the gases, was first arrived at by Gay-Lussac from chemical considerations. It is here shown to be a necessary result of the Dynamical Theory of Gases; and it is so, whatever theory we adopt as to the nature of the action between the individual molecules, as may be seen by equation (34), which is deduced from perfectly general assumptions as to the nature of the law of force.

We may therefore henceforth put $\dfrac{s_1}{s_2}$ for $\dfrac{M_1}{M_2}$, where s_1, s_2 are the specific gravities of the gases referred to a standard gas.

If we use θ to denote the temperature reckoned from absolute zero of a gas thermometer, M_0 the mass of a molecule of hydrogen, V_0^2 its mean square of velocity at temperature unity, s the specific gravity of any other gas referred to hydrogen, then the mass of a molecule of the other gas is

$$M = M_0 s; \qquad \dots \dots \quad (101)$$

its mean square of velocity,

$$V^2 = \frac{1}{s} V_0^2 \theta; \qquad \dots \dots \quad (102)$$

pressure of the gas,

$$p = \frac{1}{3} \frac{\rho}{s} \theta V_0^2. \qquad \dots \dots \quad (103)$$

We may next determine the amount of cooling by expansion.

Cooling by Expansion.

Let the expansion be equal in all directions, then

$$\frac{du}{dx} = \frac{dv}{dy} = \frac{dw}{dz} = -\frac{1}{3\rho} \frac{\partial \rho}{\partial t}, \qquad \dots \quad (104)$$

and $\dfrac{du}{dy}$ and all terms of unsymmetrical form will be zero.

If the mass of gas is of the same temperature throughout, there will be no conduction of heat, and the equation (94) will become

$$\tfrac{1}{2}\rho\beta \frac{\partial \overline{V^2}}{t} - \tfrac{1}{3}\overline{V^2}\frac{\partial \rho}{\partial t} = 0, \qquad \dots \dots \quad (105)$$

or

$$2\frac{\partial\rho}{\rho} = 3\beta\frac{\partial\overline{V^2}}{\overline{V}} = 3\beta\frac{\partial\theta}{\theta}, \quad \cdots \quad (106)$$

or

$$\frac{\partial\theta}{\theta} = \frac{2}{3\beta}\frac{\partial\rho}{\rho}, \quad \cdots \quad \cdots \quad (107)$$

which gives the relation between the density and the temperature in a gas expanding without exchange of heat with other bodies. We also find

$$\frac{\partial p}{p} = \frac{\partial\rho}{\rho} + \frac{\partial\theta}{\theta}$$

$$= \frac{2+3\beta}{3\beta}\frac{\partial\rho}{\rho}, \quad \cdots \quad \cdots \quad (108)$$

which gives the relation between the pressure and the density.

Specific Heat of Unit of Mass of Constant Volume.

The total energy of agitation of unit of mass is $\beta V^2 = E$, or

$$E = \frac{3\beta}{2}\frac{p}{\rho}. \quad \cdots \quad \cdots \quad (109)$$

If, now, additional energy in the form of heat be communicated to it without changing its density,

$$\partial E = \frac{3\beta}{2}\frac{\partial p}{\rho} = \frac{3\beta}{2}\frac{p}{\rho}\frac{\partial\theta}{\theta}. \quad \cdots \quad (110)$$

Hence the specific heat of unit of mass of constant volume is in dynamical measure

$$\frac{\partial E}{\partial\theta} = \frac{3\beta}{2}\frac{p}{\rho\theta}. \quad \cdots \quad \cdots \quad (111)$$

Specific Heat of Unit of Mass at Constant Pressure.

By the addition of the heat ∂E the temperature was raised $\partial\theta$ and the pressure ∂p. Now, let the gas expand without communication of heat till the pressure sinks to its former value, and let the final temperature be $\theta + \partial'\theta$. The temperature will thus sink by a quantity $\partial\theta - \partial'\theta$, such that

$$\frac{\partial\theta - \partial'}{\theta} = \frac{2}{2+3\beta}\frac{\partial p}{p} = \frac{2}{2+3\beta}\frac{\partial\theta}{\theta},$$

whence

$$\frac{\partial'\theta}{\theta} = \frac{3\beta}{2+3\beta}\frac{\partial\theta}{\theta}; \quad \cdots \quad \cdots \quad (112)$$

and the specific heat of unit of mass at constant pressure is

$$\frac{\partial E}{\partial' \theta} = \frac{2 + 3\beta}{2} \frac{p}{\rho \theta} \quad \cdots \cdots \quad (113)$$

The ratio of the specific heat at constant pressure to that of constant volume is known in several cases from experiment. We shall denote this ratio by

$$\gamma = \frac{2 + 3\beta}{3\beta}, \quad \cdots \cdots \quad (114)$$

whence

$$\beta = \tfrac{2}{3} \frac{1}{\gamma - 1}. \quad \cdots \cdots \quad (115)$$

The specific heat of unit of volume in ordinary measure is at constant volume

$$\frac{1}{\gamma - 1} \frac{p}{J\theta}, \quad \cdots \cdots \quad (116)$$

and at constant pressure

$$\frac{\gamma}{\gamma - 1} \frac{p}{J\theta}, \quad \cdots \cdots \quad (117)$$

where J is the mechanical equivalent of unit of heat.

From these expressions Dr. Rankine[*] calculated the specific heat of air, and found the result to agree with the value afterwards determined experimentally by M. Regnault[†].

Thermal Effects of Diffusion.

If two gases are diffusing into one another, then, omitting the terms relating to heat generated by friction and to conduction of heat, the equation (94) gives

$$\begin{aligned}
&\tfrac{1}{2}\rho_1 \frac{\partial}{\partial t} \beta_1 (\xi_1^2 + \eta_1^2 + \zeta_1^2) + \tfrac{1}{2}\rho_2 \frac{\partial}{\partial t} \beta_2 (\xi_2^2 + \eta_2^2 + \zeta_2^2) \\
&+ p_1 \left(\frac{du_1}{dx} + \frac{dv_1}{dy} + \frac{dw_1}{dz} \right) + p_2 \left(\frac{du_2}{dx} + \frac{dv_2}{dy} + \frac{dw_2}{dz} \right) \\
&= k\rho_1 \rho_2 A_1 \{ (u_1 - u_2)^2 + (v_1 - v_2)^2 + (w_1 - w_2)^2 \} \cdots
\end{aligned} \quad (118)$$

By comparison with equations (78), (79), the right-hand side of this equation becomes

$$\begin{aligned}
&X(\rho_1 u_1 + \rho_2 u_2) + Y(\rho_1 v_1 + \rho_2 v_2) + Z(\rho_1 w_1 + \rho_2 w_2) \\
&- \left(\frac{dp_1}{dx} u_1 + \frac{dp_1}{dy} v_1 + \frac{dp_1}{dz} w_1 \right) - \left(\frac{dp_2}{dx} u_2 + \frac{dp_2}{dy} v_2 + \frac{dp_2}{dz} w_2 \right) \\
&- \tfrac{1}{2}\rho_1 \frac{\partial}{\partial t} (u_1^2 + v_1^2 + w_1^2) - \tfrac{1}{2}\rho_2 \frac{\partial}{\partial t} (u_2^2 + v_2^2 + w_2^2).
\end{aligned}$$

[*] Transactions of the Royal Society of Edinburgh, vol. xx. (1850).
[†] *Comptes Rendus*, 1853.

The equation (118) may now be written

$$
\begin{aligned}
\tfrac{1}{2}\rho_1 \frac{\partial}{\partial t}&\left(u_1{}^2+v_1{}^2+w_1{}^2+\beta_1(\xi_1{}^2+\eta_1{}^2+\zeta_1{}^2)\right) \\
+\tfrac{1}{2}\rho_2 \frac{\partial}{\partial t}&\left(u_2{}^2+v_2{}^2+w_2{}^2+\beta_2(\xi_2{}^2+\eta_2{}^2+\zeta_2{}^2)\right) \\
=\mathrm{X}&(\rho_1 u_1+\rho_2 u_2)+\mathrm{Y}(\rho_1 v_1+\rho_2 v_2)+\mathrm{Z}(\rho_1 w_1+\rho_2 w_2) \\
&-\left(\frac{d \cdot pu}{dx}+\frac{d \cdot pv}{dy}+\frac{d \cdot pw}{dz}\right). \qquad\qquad
\end{aligned} \quad (119)
$$

The whole increase of energy is therefore that due to the action of the external forces *minus* the cooling due to the expansion of the mixed gases. If the diffusion takes place without alteration of the volume of the mixture, the heat due to the mutual action of the gases in diffusion will be exactly neutralized by the cooling of each gas as it expands in passing from places where it is dense to places where it is rare.

Determination of the Inequality of Pressure in different directions due to the Motion of the Medium.

Let us put
$$\rho_1\xi_1{}^2=p_1+q_1 \text{ and } \rho_2\xi_2{}^2=p_2+q_2. \quad . \quad . \quad (120)$$

Then, by equation (52),

$$
\begin{aligned}
\frac{\delta q_1}{\delta t}=&-3k_1\mathrm{A}_2\rho_1 q_1-\frac{k}{\mathrm{M}_1+\mathrm{M}_2}(2\mathrm{M}_1\mathrm{A}_1+3\mathrm{M}_2\mathrm{A}_2)\rho_2 q_1 \\
&-k(3\mathrm{A}_2-2\mathrm{A}_1)\frac{\mathrm{M}_1}{\mathrm{M}_1+\mathrm{M}_2}\rho_1 q_2-k\rho_1\rho_2\frac{\mathrm{M}_2}{\mathrm{M}_1+\mathrm{M}_2}\mathrm{A}_2 \\
&-\frac{2}{3}\mathrm{A}_1)(\overline{2u_1-u_2}^2-\overline{v_1-v_2}^2-\overline{w_1-w_2}^2), \quad . \quad . \quad
\end{aligned} \quad (121)
$$

the last term depending on diffusion; and if we omit in equation (75) terms of three dimensions in ξ, η, ζ, which relate to conduction of heat, and neglect quantities of the form $\xi\eta\rho$ and $\rho\xi^2-p$ when not multiplied by the large coefficients k, k_1, and k_2, we get

$$\frac{\partial q}{\partial t}+2p\frac{du}{dx}-\frac{2}{3}p\left(\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz}\right)=\frac{\delta q}{\delta t}. \quad . \quad (122)$$

If the motion is not subject to any very rapid changes, as in all cases except that of the propagation of sound, we may neglect $\frac{\partial q}{\partial t}$. In a single system of molecules,

$$\frac{\delta q}{\delta t}=-3k\mathrm{A}_2\rho q, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (123)$$

whence

$$q = -\frac{2p}{3k\mathrm{A}_2\rho}\left\{\frac{du}{dx} - \frac{1}{3}\left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz}\right)\right\}. \quad (124)$$

If we make

$$\frac{1}{3}\frac{1}{k\mathrm{A}_2}\frac{p}{\rho} = \mu, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (125)$$

μ will be the coefficient of viscosity, and we shall have, by equation (120),

$$\rho\xi^2 = p - 2\mu\left\{\frac{du}{dx} - \frac{1}{3}\left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz}\right)\right\},$$
$$\rho\eta^2 = p - 2\mu\left\{\frac{dv}{dy} - \frac{1}{3}\left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz}\right)\right\}, \quad \cdot \quad (126)$$
$$\rho\zeta^2 = p - 2\mu\left\{\frac{dw}{dz} - \frac{1}{3}\left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz}\right)\right\};$$

and by transformation of coordinates we obtain

$$\rho\eta\zeta = -\mu\left(\frac{dv}{dz} + \frac{dw}{dy}\right),$$
$$\rho\zeta\xi = -\mu\left(\frac{dw}{dx} + \frac{du}{dz}\right), \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (127)$$
$$\rho\xi\eta = -\mu\left(\frac{du}{dy} + \frac{dv}{dx}\right).$$

These are the values of the normal and tangential stresses in a simple gas when the variation of motion is not very rapid, and when μ, the coefficient of viscosity, is so small that its square may be neglected.

Equations of Motion corrected for Viscosity.

Substituting these values in the equation of motion (76), we find

$$\rho\frac{\partial u}{\partial t} + \frac{dp}{dx} - \mu\left\{\frac{d^2u}{dx^2} + \frac{d^2u}{dy^2} + \frac{d^2u}{dz^2}\right\}$$
$$-\frac{1}{3}\mu\frac{d}{dx}\left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz}\right) = \mathrm{X}\rho, \quad \cdot \quad \cdot \quad (128)$$

with two other equations which may be written down from symmetry. The form of these equations is identical with that of those deduced by Poisson * from the theory of elasticity, by supposing the strain to be continually relaxed at a rate proportional to its

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* *Journal de l'École Polytechnique,* 1829, vol. xiii. chap. xx. p. 139.

amount. The ratio of the third and fourth terms agrees with that given by Professor Stokes*.

If we suppose the inequality of pressure which we have denoted by q to exist in the medium at any instant, and not to be maintained by the motion of the medium, we find, from equation (123),

$$q_1 = C e^{-3kA_2\rho t} \quad . \quad . \quad . \quad . \quad . \quad . \quad (129)$$

$$= C e^{-\frac{t}{T}} \text{ if } T = \frac{1}{3kA_2\rho} = \frac{\mu}{p}; \quad . \quad . \quad (130)$$

the stress q is therefore relaxed at a rate proportional to itself, so that

$$\frac{\delta q}{q} = \frac{\delta t}{T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (131)$$

We may call T the modulus of the time of relaxation.

If we next make $k=0$, so that the stress q does not become relaxed, the medium will be an elastic solid, and the equation

$$\frac{\partial(\rho\xi^2 - p)}{\partial t} + 2p\frac{du}{dx} - \frac{2}{3}p\left(\frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz}\right) = 0 \quad . \quad (132)$$

may be written

$$\frac{\partial}{\partial t}\left\{(p_{xx} - p) + 2p\frac{d\alpha}{dx} - \frac{2}{3}p\left(\frac{d\alpha}{dx} + \frac{d\beta}{dy} + \frac{d\gamma}{dz}\right)\right\} = 0, \quad . \quad (133)$$

where α, β, γ are the displacements of an element of the medium, and p_{xx} is the normal pressure in the direction of x. If we suppose the initial value of this quantity zero, and p_{xx} originally equal to p, then, after a small displacement,

$$p_{xx} = p - p\left(\frac{d\alpha}{dx} + \frac{d\beta}{dy} + \frac{d\gamma}{dz}\right) - 2p\frac{d\alpha}{dx}; \quad . \quad (134)$$

and by transformation of coordinates the tangential pressure

$$p_{xy} = -p\left(\frac{d\alpha}{dy} + \frac{d\beta}{dx}\right). \quad . \quad . \quad . \quad . \quad (135)$$

The medium has now the mechanical properties of an elastic solid, the rigidity of which is p, while the cubical elasticity is $\frac{5}{3}p$†.

The same result and the same ratio of the elasticities would be obtained if we supposed the molecules to be at rest, and to act on one another with forces depending on the distance, as in the statical molecular theory of elasticity. The coincidence of the properties of a medium in which the molecules are held in equilibrium by attractions and repulsions, and those of a medium

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* " On the Friction of Fluids in Motion and the Equilibrium and Motion of Elastic Solids," Cambridge Phil. Trans. vol. viii. (1845), p. 297, equation (12).

† Ibid. p. 311, equation (29).

in which the molecules move in straight lines without acting on each other at all, deserves notice from those who speculate on theories of physics.

The fluidity of our medium is therefore due to the mutual action of the molecules, causing them to be deflected from their paths.

$$\left.\begin{array}{l}\text{The coefficient of instantaneous rigidity of a gas is}\\ \qquad\text{therefore } p. \\ \text{The modulus of the time of relaxation is T.}\\ \text{The coefficient of viscosity is } \mu = p\text{T.}\end{array}\right\} \quad (136)$$

Now p varies as the density and temperature conjointly, while T varies inversely as the density.

Hence μ varies as the absolute temperature, and is independent of the density.

This result is confirmed by the experiments of Mr. Graham on the Transpiration of Gases[*], and by my own experiments on the Viscosity or Internal Friction of Air and other Gases[†].

The result, that the viscosity is independent of the density, follows from the Dynamical Theory of Gases, whatever be the law of force between the molecules. It was deduced by myself[‡] from the hypothesis of hard elastic molecules, and M. O. E. Meyer[§] has given a more complete investigation on the same hypothesis.

The experimental result, that the viscosity is proportional to the absolute temperature, requires us to abandon this hypothesis, which would make it vary as the square root of the absolute temperature, and to adopt the hypothesis of a repulsive force inversely as the fifth power of the distance between the molecules, which is the only law of force which gives the observed result.

Using the foot, the grain, and the second as units, my experiments give, for the temperature of 62° Fahr., and in dry air,

$$\mu = 0\cdot0936.$$

If the pressure is 30 inches of mercury, we find, using the same units,

$$p = 477360000.$$

Since $p\text{T} = \mu$, we find that the modulus of the time of relaxation of rigidity in air of this pressure and temperature is

$$\frac{1}{5099100000} \text{ of a second.}$$

This time is exceedingly small, even when compared with the

* Philosophical Transactions, 1846 and 1849.
† Proceedings of the Royal Society, February 8, 1866; Philosophical Transactions, 1866, p. 249.
‡ Philosophical Magazine, January 1860.
§ Poggendorff's *Annalen*, 1865.

period of vibration of the most acute audible sounds; so that even in the theory of sound we may consider the motion as steady during this very short time, and use the equations we have already found, as has been done by Professor Stokes[*].

Viscosity of a Mixture of Gases.

In a complete mixture of gases, in which there is no diffusion going on, the velocity at any point is the same for all the gases. Putting

$$\frac{2}{3}\left(2\frac{du}{dx} - \frac{dv}{dy} - \frac{dw}{dz}\right) = U, \quad \ldots \quad (137)$$

equation (122) becomes

$$\left.\begin{array}{l} p_1 U = -3k_1 A_2 \rho_1 q_1 - \dfrac{k}{M_1 + M_2}(2M_1 A_1 + 3M_2 A_2)\rho_2 q \\[2mm] \qquad - k(3A_2 - 2A_1)\dfrac{M_2}{M_1 + M_2}\rho_1 q_2. \quad \ldots \end{array}\right\} \quad (138)$$

Similarly

$$\left.\begin{array}{l} p_2 U = -3k_2 A_2 \rho_2 q_2 - \dfrac{k}{M_1 + M_2}(2M_2 A_1 + 3M_1 A_2)\rho_1 q_2 \\[2mm] \qquad - k(3A_2 - 2A_1)\dfrac{M_1}{M_1 + M_2}\rho_2 q_1. \quad \ldots \end{array}\right\} \quad (139)$$

Since $p = p_1 + p_2$ and $q = q_1 + q_2$, where p and q refer to the mixture, we shall have

$$\mu U = -q = -(q_1 + q_2),$$

where μ is the coefficient of viscosity of the mixture.

If we put s_1 and s_2 for the specific gravities of the two gases, referred to a standard gas, in which the values of p and ρ at temperature θ_0 are p_0 and ρ_0,

$$\mu = \frac{p_0 \theta}{\rho_0 \theta_0} \cdot \frac{Ep_1^2 + Fp_1 p_2 + Gp_2^2}{3A_2 k_1 s_1 E p_1^2 + H p_1 p_2 + 3A_2 k_2 s_2 G p_2^2}, \quad (140)$$

where μ is the coefficient of viscosity of the mixture, and

$$\left.\begin{array}{l} E = \dfrac{ks_1}{s_1 + s_2}(2s_2 A_1 + 3s_1 A_2), \\[2mm] F = 3A_2(k_1 s_1 + k_2 s_2) - (3A_2 - 2A_1)k\,\dfrac{2s_1 s_2}{s_1 + s_2}, \\[2mm] G = \dfrac{ks_2}{s_1 + s_2}(2s_1 A_1 + 3s_2 A_2), \\[2mm] H = 3A_2 s_1 s_2\{3k_1 k_2 A_2 + 2k^2 A_1\}. \end{array}\right\} \quad (141)$$

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[*] "On the effect of the Internal Friction of Fluids on the motion of Pendulums," Cambridge Transactions, vol. ix. (1850), art. 79.

This expression is reduced to μ_1 when $p_2 = 0$, and to μ_2 when $p_1 = 0$. For other values of p_1 and p_2 we require to know the value of k, the coefficient of mutual interference of the molecules of the two gases. This might be deduced from the observed values of μ for mixtures; but a better method is by making experiments on the interdiffusion of the two gases. The experiments of Graham on the transpiration of gases, combined with my experiments on the viscosity of air, give as values of k_1 for air, hydrogen, and carbonic acid :—

$$\text{Air} \quad \ldots \quad k_1 = \quad 4{\cdot}81 \times 10^{10},$$
$$\text{Hydrogen} \quad \ldots \quad k_1 = 142{\cdot}8 \quad \times 10^{10},$$
$$\text{Carbonic acid} \quad \ldots \quad k_1 = \quad 3{\cdot}9 \quad \times 10^{10}.$$

The experiments of Graham in 1863, referred to at page 199, on the interdiffusion of air and carbonic acid, give the coefficient of mutual interference of these gases,

$$\text{Air and carbonic acid} \quad \ldots \quad k = 5{\cdot}2 \times 10^{10};$$

and by taking this as the absolute value of k, and assuming that the ratios of the coefficients of interdiffusion given at page 202 are correct, we find

$$\text{Air and hydrogen} \quad \ldots \quad k = 29{\cdot}8 \times 10^{10}.$$

These numbers are to be regarded as doubtful, as we have supposed air to be a simple gas in our calculations, and we do not know the value of k between oxygen and nitrogen. It is also doubtful whether our method of calculation applies to experiments such as the earlier observations of Mr. Graham.

I have also examined the transpiration-times determined by Graham for mixtures of hydrogen and carbonic acid, and hydrogen and air, assuming a value of k roughly, to satisfy the experimental results about the middle of the scale. It will be seen that the calculated numbers for hydrogen and carbonic acid exhibit the peculiarity observed in the experiments, that a small addition of hydrogen *increases* the transpiration-time of carbonic acid, and that in both series the times of mixtures depend more on the slower than on the quicker gas.

The assumed values of k in these calculations were—

$$\text{For hydrogen and carbonic acid} \quad k = 12{\cdot}5 \times 10^{10},$$
$$\text{For hydrogen and air} \quad \ldots \quad k = 18{\cdot}8 \times 10^{10};$$

and the results of observation and calculation are, for the times of transpiration of mixtures of

Hydrogen and Carbonic acid.		Observed.	Calculated.	Hydrogen and Air.		Observed.	Calculated.
100	0	·4321	·4375	100	0	·4434	·4375
97·5	2·5	·4714	·4750	95	5	·5282	·5300
95	5	·5157	·5089	90	10	·5880	·6028
90	10	·5722	·5678	75	25	·7488	·7438
75	25	·6786	·6822	50	50	·8179	·8488
50	50	·7339	·7652	25	75	·8790	·8946
25	75	·7535	·7468	10	90	·8880	·8983
10	90	·7521	·7361	5	95	·8960	·8996
0	100	·7470	·7272	0	100	·9000	·9010

The numbers given are the ratios of the transpiration-times of mixtures to that of oxygen as determined by Mr. Graham, compared with those given by the equation (140) deduced from our theory.

Conduction of Heat in a Single Medium (γ).

The rate of conduction depends on the value of the quantity
$$\tfrac{1}{2}\beta\rho(\xi^3 + \xi\eta^2 + \xi\zeta^2),$$
where ξ^3, $\xi\eta^2$, and $\xi\zeta^2$ denote the mean values of those functions of ξ, η, ζ for all the molecules in a given element of volume.

As the expressions for the variations of this quantity are somewhat complicated in a mixture of media, and as the experimental investigation of the conduction of heat in gases is attended with great difficulty, I shall confine myself here to the discussion of a single medium.

Putting

$$Q = M(u+\xi)\{u^2 + v^2 + w^2 + 2u\zeta + 2v\eta + 2w\zeta \\ + \beta(\xi^2 + \eta^2 + \zeta^2)\}, \quad \ldots \ldots \quad (142)$$

and neglecting terms of the forms $\xi\eta$ and ξ^3 and $\xi\eta^2$ when not multiplied by the large coefficient k_1, we find by equations (75), (77), and (54),

$$\left.\begin{aligned}
\rho\frac{\partial}{\partial t}\beta(\xi^3 + \xi\eta^2 + \xi\zeta^2) + \beta\frac{d}{dx}\cdot\rho(\xi^4 + \xi^2\eta^2 + \xi^2\zeta^2) \\
-\beta(\xi^2 + \eta^2 + \zeta^2)\frac{dp}{dx} - 2\beta\xi^2\frac{dp}{dx} \\
= -3k_1\rho^2 A_2\beta\{\xi^3 + \xi\eta^2 + \xi\zeta^2\}. \quad \ldots
\end{aligned}\right\} \quad (143)$$

The first term of this equation may be neglected, as the rate of conduction will rapidly establish itself. The second term contains quantities of four dimensions in ξ, η, ζ, whose values will depend on the distribution of velocity among the molecules. If the distribution of velocity is that which we have proved to exist

when the system has no external force acting on it, and has arrived at its final state, we shall have, by equations (29), (31), (32),

$$\overline{\xi^4} = 3\overline{\xi^2}\cdot\overline{\xi^2}, = 3\frac{p^2}{\rho^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (144)$$

$$\overline{\xi^2\eta^2} = \overline{\xi^2}\cdot\overline{\eta^2} = \frac{p^2}{\rho^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (145)$$

$$\overline{\xi^2\zeta^2} = \overline{\xi^2}\cdot\overline{\zeta^2} = \frac{p^2}{\rho^2}; \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (146)$$

and the equation of conduction may be written

$$5\beta\frac{p^2}{\rho\theta}\frac{d\theta}{dx} = -3k_1\rho^2\mathrm{A}_2\beta\{\xi^3 + \xi\eta^2 + \xi\zeta^2\}. \quad \cdot \quad (147)$$

[Addition made December 17, 1866.]

[*Final Equilibrium of Temperature.*]

[The left-hand side of equation (147), as sent to the Royal Society, contained a term $2(\beta-1)\frac{p}{\rho}\frac{dp}{dx}$, the result of which was to indicate that a column of air, when left to itself, would assume a temperature varying with the height, and greater above than below. The mistake arose from an error* in equation (143). Equation (147), as now corrected, shows that the flow of heat depends on the variation of temperature only, and not on the direction of the variation of pressure. A vertical column would therefore, when in thermal equilibrium, have the same temperature throughout.

When I first attempted this investigation I overlooked the fact that $\overline{\xi^4}$ is not the same as $\overline{\xi^2}\cdot\overline{\xi^2}$, and so obtained as a result that the temperature diminishes as the height increases at a greater rate than it does by expansion when air is carried up in mass. This leads at once to a condition of instability, which is inconsistent with the second law of thermodynamics. I wrote to Professor Sir W. Thomson about this result, and the difficulty I had met with, but presently discovered *one* of my mistakes, and arrived at the conclusion that the temperature would increase with the height. This does not lead to mechanical instability, or to any self-acting currents of air, and I was in some degree satisfied with it. But it is equally inconsistent with the second law of thermodynamics. In fact, if the temperature of any substance, when in thermic equilibrium, is a function of the height, that of any other substance must be the same function of the height. For if not, let equal columns of the two substances be

* The last term on the left-hand side was not multiplied by β.

enclosed in cylinders impermeable to heat, and put in thermal communication at the bottom. If, when in thermal equilibrium, the tops of the two columns are at different temperatures, an engine might be worked by taking heat from the hotter and giving it up to the cooler, and the refuse heat would circulate round the system till it was all converted into mechanical energy, which is in contradiction to the second law of thermodynamics.

The result as now given is, that temperature in gases, when in thermal equilibrium, is independent of height, and it follows from what has been said that temperature is independent of height in all other substances.

If we accept this law of temperature as the actual one, and examine our assumptions, we shall find that, unless $\overline{\xi^4} = 3\overline{\xi^2} \cdot \overline{\xi^2}$, we should have obtained a different result. Now this equation is derived from the law of distribution of velocities to which we were led by independent considerations. We may therefore regard this law of temperature, if true, as in some measure a confirmation of the law of distribution of velocities.]

Coefficient of Conductivity.

If C is the coefficient of conductivity of the gas for heat, then the quantity of heat which passes through unit of area in unit of time measured as mechanical energy, is

$$C \frac{d\theta}{dx} = \frac{5}{6} \frac{\beta}{k_1 A_2} \frac{p^2}{\rho^2 \theta} \frac{d\theta}{dx} \quad \cdots \cdots \quad (148)$$

by equation (147).

Substituting for β its value in terms of γ by equation (115), and for k_1 its value in terms of μ by equation (125), and calling p_0, ρ_0, and θ_0 the simultaneous pressure, density, and temperature of the standard gas, and s the specific gravity of the gas in question, we find

$$C = \frac{5}{3(\gamma - 1)} \frac{p_0}{\rho_0 \theta_0} \frac{\mu}{s}. \quad \cdots \cdots \quad (149)$$

For air we have $\gamma = 1 \cdot 409$, and, at the temperature of melting ice, or $274° \cdot 6$ C. above absolute zero, $\sqrt{\dfrac{p}{\rho}} = 918 \cdot 6$ feet per second, and at $16° \cdot 6$ C., $\mu = 0 \cdot 0936$ in foot-grain-second measure. Hence for air at $16° \cdot 6$ C. the conductivity for heat is

$$C = 1172. \quad \cdots \cdots \quad (150)$$

That is to say, a horizontal stratum of air one foot thick, of which the upper surface is kept at $17°$ C., and the lower at $16°$ C., would

in one second transmit through every square foot of horizontal surface a quantity of heat the mechanical energy of which is equal to that of 2344 grains moving at the rate of one foot per second.

Principal Forbes[*] has deduced from his experiments on the conduction of heat in bars, that a plate of wrought iron one foot thick, with its opposite surfaces kept $1°$ C. different in temperature, would, when the mean temperature is $25°$ C., transmit in one minute through every square foot of surface as much heat as would raise one cubic foot of water $0°·0127$ C.

Now the dynamical equivalent in foot-grain-second measure of the heat required to raise a cubic foot of water $1°$ C. is $1·9157 \times 10^{10}$.

It appears from this that iron at $25°$ C. conducts heat 3525 times better than air at $16°·6$ C.

M. Clausius, from a different form of the theory, and from a different value of μ, found that lead should conduct heat 1400 times better than air. Now iron is twice as good a conductor of heat as lead, so that this estimate is not far different from that of M. Clausius in actual value.

In reducing the value of the conductivity from one kind of measure to another we must remember that its dimensions are MLT^{-3}, when expressed in absolute dynamical measure.

Since all the quantities which enter into the expression for C are constant except μ, the conductivity is subject to the same laws as the viscosity; that is, it is independent of the pressure, and varies directly as the absolute temperature. The conductivity of iron diminishes as the temperature increases.

Also, since γ is nearly the same for air, oxygen, hydrogen, and carbonic oxide, the conductivity of these gases will vary as the ratio of the viscosity to the specific gravity. Oxygen, nitrogen, carbonic oxide, and air will have equal conductivity, while that of hydrogen will be about seven times as great.

The value of γ for carbonic acid is $1·27$; its specific gravity is $\frac{11}{8}$ of that of oxygen, and its viscosity $\frac{8}{11}$ of that of oxygen. The conductivity of carbonic acid for heat is therefore about $\frac{7}{9}$ of that of oxygen or of air.

[*] "Experimental Inquiry into the Laws of the Conduction of Heat in Bars," Edinburgh Transactions, 1861–62.

XXIII. *Addendum to Contributions to the Mineralogy of Nova Scotia. By* Professor How *.

III. *On Borates in Gypsum and Anhydrite.*

MY attention has been drawn by Principal Dawson to some particulars mentioned in the paper named above which I shall be glad to state; at the same time I am enabled to give some interesting facts he has kindly communicated, and take the opportunity of giving an analysis of gypsum bearing on one of them, and of adding a few remarks on other points.

In the first place I have inadvertently named *Cape* Canseau as a locality of plaster, I should have said the *Gut* of Canseau. The former is some thirty miles south of the latter; and, as stated by Dr. Dawson, a large part of the peninsula, terminating at Cape Canseau, is occupied by white fine-grained gneiss with veins and masses of granite; there is also much mica-slate and dark-coloured slate; it is in fact quite destitute of gypsum. The Gut of Canseau is the narrow strait between Nova Scotia proper and Cape Breton; and on the Cape-Breton side is situated Plaster Cove, where the beds referred to are seen. They are thus described in a passage of 'Acadian Geology,' which I am sorry to have overlooked at the time when it would have been of great service to me. "About two-thirds of the thickness of the bed consist of crystalline anhydrite, and the remaining third of very fine-grained common gypsum. The anhydrite prevails in the lower part of the bed, the common gypsum in the upper; but the greater part of the bed consists of an intimate mixture of both substances, the common gypsum forming a base in which minute crystals of anhydrite are scattered, and bands in which anhydrite prevails alternating with others in which common gypsum predominates." In a subsequent page (283) an explanation is given of the mode in which the gypsum and gypseous marl may have been formed from sea-water containing sulphuric acid in varying quantities, and the fact stated that anhydrite must have been deposited with the gypsum, and that it seems difficult to account for its production, unless it may have been formed by acid vapours and scattered over the bed of the sea. Dr. Dawson does not think the existence of salt proves anything as to the origin of the gypsum, as, under any probable hypothesis, the rock must have been formed in the sea, and, as the marls and sandstones seem to indicate, in limited and probably shallow basins.

In speaking of ordinary sea-water not containing the boracic acid found in the borates in plaster here, I might have referred to the interesting discovery of the acid in *limited portions* of the

* Communicated by the Author.

Pacific Ocean on the coast of California, considered by Mr. Veatch to be due to volcanic action *. Rammelsberg has detected boracic acid in sea-water and in sea-weed ; but where, I cannot say, as I have not access to his paper.

To the minerals found in gypsum, Dr. Dawson says, "I may add peroxide of iron and bituminous and carbonaceous matters." As regards the former, I should certainly have stated that it no doubt exists, and is the cause of the pink and red tints often observed, especially in fibrous gypsum. At one quarry, at Wentworth, Hants county, there is found a deep-red crystalline gypsum. With reference to the bituminous matters, I on one occasion analyzed a nearly black gypsum from near Walton, Hants county, with the following results :—

Gypsum	80·45
Anhydrite	2·84
Bituminous matter	1·53
Clay and sand	7·94
Carbonates of lime and magnesia, with alumina and oxide of iron	7·23
	100·00

Interesting additional facts are given by Dr. Dawson, who mentions that at Gay's River, Colchester county, a very singular bed of gypsum exists containing pure quartz-sand, and also that he has in his cabinet a specimen of gypsum from Cape Breton enclosing a crystal of mispickel.

With reference to the formation of gypsum from anhydrite, Dr. Dawson has long suspected, from the unusually disturbed condition of the beds near those of gypsum, that part of this rock, at least, may have resulted from absorption of water by anhydrite, or some similar process involving *increase of bulk* ; but, owing to the obscurities caused by denudation and the unequal erosion of the gypsum, he has not been able to satisfy himself fully on the subject. The whole question as to how the beds of anhydrite could have been formed he thinks well worthy of study.

XXIV. *On the Integration of the General Linear Partial Differential Equation of the Second Order. By* R. Moon, *M.A., Honorary Fellow of Queen's College, Cambridge*†.

IN a former paper‡ I pointed out the criteria which must be satisfied in order that the equation

$$0 = R \frac{d^2z}{dx^2} + S \frac{d^2z}{dx\,dy} + T \frac{d^2z}{dy^2} + V \quad . \quad . \quad . \quad (1)$$

* Chemical News, vol. iv. p. 16. † Communicated by the Author.
‡ Phil. Mag. for February 1868.

may admit of being derived from a single partial differential equation of the first order, together with the mode of ascertaining such equation in the cases in which it exists.

I now propose to show the circumstances under which (1) is derivable from a single integral equation *involving one or more arbitrary functions,* as well as the form of the integral equation when any such obtains.

Let the integral equations involve the arbitrary functions ϕ, ψ, &c. which appear in it under the forms ϕ, ϕ', $\phi''\ldots$, ψ, ψ', $\psi''\ldots$; and, solving with respect to ϕ, let it stand

$$\phi(u) = \bar{\mathrm{F}}(zyz), \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

where u is a definite function of xyz, and where $\bar{\mathrm{F}}$ may involve ϕ', ϕ'', $\ldots$, ψ, ψ', ψ'' $\ldots$, but does not involve ϕ.

Differentiating (2), we get

$$\left. \begin{aligned} 0 &= \phi'(u)\frac{du}{dx} - \mathrm{F}'(x) + \left\{ \phi'(u)\,\frac{du}{dz} - \mathrm{F}'(z) \right\}p, \\ 0 &= \phi'(u)\frac{du}{dy} - \mathrm{F}'(y) + \left\{ \phi'(u)\,\frac{du}{dz} - \mathrm{F}'(z) \right\}q. \end{aligned} \right\} \quad \cdot \quad \cdot \quad (3)$$

I shall first assume that the number of derivatives of ϕ contained in (1) is finite, and that $\phi^{(m-1)}(u)$ is the *highest* derivative; in which case each of the equations (3) will contain $\phi^{(m)}(u)$ or U* (unless, indeed, u contains x or y only, a case which I pass by for the present), so that (3) may be replaced by

$$\left. \begin{aligned} p &= \mathrm{F}(xyz\mathrm{U}), \\ q &= f(xyz\mathrm{U}), \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

whence we have

$$\frac{dp}{dx} = \mathrm{F}'(x) + \mathrm{F}'(z) + \mathrm{F}'(\mathrm{U}) \cdot \mathrm{U}_1 \cdot \left(\frac{du}{dx} + \frac{du}{dz}p \right)$$

$$= \mathrm{F}'(x) + \mathrm{F}'(z)\mathrm{F} + \mathrm{F}''(\mathrm{U}) \cdot \mathrm{U}_1 \cdot \left(\frac{du}{dx} + \frac{du}{dz}\mathrm{F} \right);$$

and putting F_x for $\mathrm{F}'(x) + \mathrm{F}'(z) \cdot \mathrm{F}$, and $\dfrac{d(u)}{dx}$ for $\dfrac{du}{dx} + \dfrac{du}{dz}\,\mathrm{F}$,

and similarly with respect to $\mathrm{F}_y f_x f_y \dfrac{d(u)}{dy}$, U_1 standing for $\phi^{(m+1)}(u)$, we shall have

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* If (2) contain no derivative of ϕ, each of the equations (3) will contain ϕ'; and putting U for ϕ' the ensuing reasoning will remain unaltered.

$$\frac{dp}{dx} = \mathrm{F}_x + \mathrm{F}'(\mathrm{U}) \cdot \mathrm{U}_1 \cdot \frac{d(u)}{dx},$$

$$\frac{dp}{dy} = \mathrm{F}_y + \mathrm{F}'(\mathrm{U}) \cdot \mathrm{U}_1 \cdot \frac{d(u)}{dy},$$

$$\frac{dq}{dx} = f_x + f'(\mathrm{U}) \cdot \mathrm{U}_1 \cdot \frac{d(u)}{dx}, \qquad \cdots \quad (5)$$

$$\frac{dq}{dy} = f_y + f'(\mathrm{U}) \cdot \mathrm{U}_1 \cdot \frac{d(u)}{dy}.$$

All the independent relations that can exist between the partial differential coefficients $\dfrac{dp}{dx}, \dfrac{dp}{dy}, \dfrac{dq}{dx}, \dfrac{dq}{dy}$, and the variables $x, y,$ $z, p, q,$ are embodied in the seven equations (2), (4), and (5); and the whole of such relations which are free from ϕ itself are comprised in equations (4) and (5). Moreover, since p and q have been eliminated from (5) by means of (4), the equations (5) embody all the relations free from ϕ which can exist between the same partial differential coefficients and the variables $x, y, z.$

But if we put $\mathrm{R}_1, \mathrm{S}_1, \mathrm{T}_1, \mathrm{V}_1$ for the values assumed by $\mathrm{R, S,}$ $\mathrm{T, V}$ when we put $\mathrm{F,} f$ for p, q respectively, we shall have, in the equations

$$0 = \mathrm{R}_1 \frac{dp}{dx} + \mathrm{S}_1 \frac{dp}{dy} + \mathrm{T}_1 \frac{dq}{dy} + \mathrm{V}_1, \qquad \cdots \quad (5a)$$

$$0 = \frac{dq}{dx} - \frac{dp}{dy},$$

two relations between the same partial differential coefficients and x, y, z which do not contain $\phi.$

Hence, if we substitute in these last the values of the partial differential coefficients given by (5), we shall have *in each case* a result which must hold identically, viz.

$$0 = \mathrm{R}_1 \mathrm{F} f_x + \mathrm{S}_1 \mathrm{F}_y + \mathrm{T}_1 \mathrm{F}_z + \mathrm{V}$$
$$+ \left\{ \mathrm{R}_1 \frac{d(u)}{dx} + \mathrm{S}_1 \frac{d(u)}{dy} \cdot \mathrm{F}'(\mathrm{U}) + \mathrm{T}_1 \frac{d(u)}{dy} f'(\mathrm{U}) \right\} \cdot \mathrm{U}_1,$$

$$0 = f - \mathrm{F}_y + \left\{ f'(\mathrm{U}) \frac{d(u)}{dx} - \mathrm{F}'(\mathrm{U}) \frac{d(u)}{dy} \right\} \mathrm{U}_1;$$

whence, since U_1 does not enter into F or f, we have

$$0 = \mathrm{R}_1 \mathrm{F}_x + \mathrm{S}_1 \mathrm{F}_y + \mathrm{T}_1 \mathrm{F}_z + \mathrm{V},$$

$$0 = \mathrm{R}_1 \frac{d(u)}{dx} + \mathrm{S}_1 \frac{d(u)}{dy} \cdot \mathrm{F}'(\mathrm{U}) + \mathrm{T}_1 \frac{d(u)}{dy} f'(\mathrm{U}),$$

$$0 = f_x - \mathrm{F}_y, \qquad \cdots \quad (6)$$

$$0 = f'(\mathrm{U}) \frac{d(u)}{dx} - \mathrm{F}'(\mathrm{U}) \frac{d(u)}{dy}.$$

The second and fourth of these, (6ii) and (6iv), give us

$$0 = R_1 \overline{\frac{d(u)}{dx}}\Big|^2 + S_1 \frac{d(u)}{dx}\frac{d(u)}{dy} + T_1 \overline{\frac{d(u)}{dy}}\Big|^2 ;$$

therefore if m_1, m_2 be the roots of the equation

$$0 = Rm^2 + Sm + T,$$

we shall have

$$0 = \frac{d(u)}{dx} - m_1 \frac{d(u)}{dy},$$

$$0 = F'(U) - m f'(U).$$

Integrating the last, we get, since m_1 does not contain U,

$$F(xyzU) = m_1 f(xyzU) + f_a(xyz),$$

where f_a does not contain U or higher derivatives of ϕ, but may contain lower derivatives of ϕ.

Hence we have

$$F_x = m_1 f_x + \frac{d(m_1)}{dx}\cdot f + f_{ax},$$

$$F_y = m_1 f_y + \frac{d(m_1)}{dy}\cdot f + f_{ay},$$

where

$$f_{ax} = f_a'(x) + f_a'(z)\cdot f = f_a'(x) + (m_1 f + f_a)\cdot f_a'(z),$$

$$f_{ay} = f_a'(y) + f_a'(z)\cdot f.$$

Substituting these values, (6i) and (6iii) become

$$\left.\begin{array}{l}0 = R_1\left\{ m_1 f_x + \dfrac{d(m_1)}{dx}\cdot f + f_{ax}\right\} + S_1\left\{ m_1 f_y + \dfrac{d(m_1)}{dy}\cdot f + f_{ay}\right\} \\[2mm] \qquad + T_1 f_y + V_1, \\[2mm] 0 = m_1 f_y - f_x + f_{ay} + \dfrac{d(m_1)}{dy} f.\end{array}\right\} \quad (7)$$

Dividing by R_1, putting $-\overline{m_1 + m_2}$ for $\dfrac{S_1}{R_1}$, and $m_1 m_2$ for $\dfrac{T_1}{R_1}$, the first of these becomes, taking account of the value of $m_1 f_y - f_x$ given by the second,

$$0 = f_{ax} - m_2 f_{ay} + \left\{ \frac{d(m_1)}{dx} - m_2 \frac{d(m_1)}{dy}\right\}\cdot f + \frac{V_1}{R_1}.$$

Suppose, now, that $\dfrac{V}{R}$ is of the form $\alpha p + \beta q + \gamma z + \delta$, and R, S, T, V, α, β, γ, δ are functions of x and y only; and the last

equation becomes

$$0 = f_{ax} - m_2 f_{ay} + \alpha f_a \left\{ m_1 \alpha + \beta + \frac{d(m_1)}{dx} - m_2 \frac{d(m_1)}{dy} \right\} \cdot f + \gamma z + \delta;$$

and if we put for f_{ax}, f_{ay} the above values, we shall have in the case now being considered, instead of equations (7),

$$\left. \begin{aligned} 0 = {} & f_a'(x) - m_2 f_a'(y) + f_a \cdot f_a'(z) + \alpha f_a + \gamma z + \delta \\ & + \left\{ \overline{m_1 - m_2} \cdot f_a'(z) + m_1 \alpha + \beta + \frac{dm_1}{dx} - m_2 \frac{dm_1}{dy} \right\} \cdot f, \\ 0 = {} & m_1 f_y - f_x + f_{ay} + \frac{d(m_1)}{dy} \cdot f. \end{aligned} \right\} \quad (8)$$

Two cases occur.

I. Suppose that f_a, which does not contain $\phi^{(m)}$ (*i. e.* U) or *higher* derivatives of ϕ, is also destitute of $\phi^{(m-1)}$.

In this case $f_a, f_a'(x), f_a'(y), f_a'(z)$ are alike free from U; but f contains U; hence the coefficient of f in the first of equations (8) must vanish, *i. e.* we must have

$$0 = f_a'(x) - m_2 f_a'(y) + f_a \cdot f_a'(z) + \alpha f_a + \gamma z + \delta, \quad \cdot \quad \cdot \quad (9)$$

$$0 = (m_1 - m_2) f_a'(z) + m_1 \alpha + \beta + \frac{dm_1}{dx} - m_2 \frac{dm_1}{dy}.$$

From the latter we have

$$f_a'(z) = \mu,$$

where

$$\mu = \frac{1}{m_2 - m_1} \left\{ m_1 \alpha + \beta + \frac{dm_1}{dx} - m_2 \frac{dm_1}{dy} \right\}.$$

Hence

$$f_a = \mu z + f_b(xy); \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

and substituting this in (9), observing that

$$f_a'(x) = \frac{d\mu}{dx} z + f_b'(x),$$

$$f_a'(y) = \frac{d\mu}{dy} z + f_b'(y),$$

$$f_a'(z) = \mu,$$

we get the result,

$$0 = f_b'(x) - m_2 f_b'(y) + \overline{\mu + \alpha} \cdot f_b + \delta$$
$$+ z \left\{ \frac{d\mu}{dx} - m_2 \frac{d\mu}{dy} + \mu \cdot \overline{\mu + \alpha} + \gamma \right\},$$

in which, since f_b contains xy only, the coefficient of z must va-

nish.　Hence we have simultaneously

$$0 = f_b{}'(x) - m_2 f_b{}'(y) + (\mu + \alpha) f_b + \delta, \quad . \quad . \quad (11),$$

$$0 = \frac{d\mu}{dx} - m_2 \frac{d\mu}{dy} + \mu(\mu + \alpha) + \gamma ;$$

the last of which is an equation of condition which must be satisfied by the coefficients of the given equation in order that the latter may admit of an integral of the kind treated of in this paper, under the circumstances we are now considering, *i. e.* when f_a does not involve U_{-1}.

A reference to my former paper will show, it being observed that the m there used is the reciprocal of that above employed, that the above equation of condition is identical with that which must be satisfied in order that the given equation may be capable of being derived from a single partial differential equation of the first order.　Also

$$\mathrm{F} = m_1 f + f_a = m_1 f + \mu z + f_b ;$$

in other words,　$0 = p - m_1 q - \mu z - f_b, \quad . \quad . \quad . \quad . \quad . \quad (12)$

where f_b is determined by (11).　My former paper shows that (12) is the single partial differential equation of the first order from which, the condition being satisfied, the given equation is derivable.

II. But if f_a contains $\phi^{(m-1)}$ or U_{-1}, the process must be modified.　In this case, if

$$f_a(xyz) = f_\alpha(xyz U_{-1})*,$$

we shall have

$$f_a{}'(x) = f_\alpha{}'(x) + f_\alpha{}'(U_{-1}) . U . \frac{du}{dx},$$

$$f_a{}'(y) = f_\alpha{}'(y) + f_\alpha{}'(U_{-1}) . U . \frac{du}{dy},$$

$$f_a{}'(z) = f_\alpha{}'(z),$$

since $\dfrac{du}{dz} = 0\dagger$.

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* Note throughout that when a symbol is used as a subscribed index, and also as a symbol of quantity, no connexion exists between the two modes of user.

† This appears thus : $\dfrac{d(u)}{dx} - m_1 \dfrac{d(u)}{dy} = 0$ is equivalent to

$$\frac{dz}{dx} - m_1 \frac{dz}{dy} + \mathrm{F}_1(xyz) = 0 ,$$

the integral of which, when m_1 involves x and y only, will always be of the form
$$z = \text{funct.} \{x, y, \phi(\omega)\},$$
where $\omega = $ a const. is the integral of $0 = dy + m_1 dx$; whence it appears that the assumption that $\dfrac{du}{dz}$ does not vanish leads us to an integral relation between x, y, z different from that which we are now supposing to exist.

Hence (8^i) becomes, putting $m_1 \dfrac{du}{dy}$ for $\dfrac{du}{dx}$,

$$0 = f'_\alpha(x) - m_2 f'_\alpha(y) + f_\alpha . f'_\alpha(z) + \alpha f_\alpha + \gamma z + \delta$$

$$+ \overline{m_1 - m_2} . \frac{du}{dy} . f'_\alpha(U_{-1}) . U$$

$$+ \left\{ \overline{m_1 - m_2} . f'_\alpha(z) + m_1 \alpha + \beta + \frac{dm_1}{dx} - m_2 \frac{dm_1}{dy} \right\} . f.$$

Now f_α, $f'_\alpha(x)$, $f'_\alpha(y)$, $f'_\alpha(z)$ are all free from U, while f contains U.

If f contains U otherwise than in the simple power, the coefficient of f in the last equation must vanish, since no other term contains U otherwise than in the simple power.

Moreover, if the coefficient of f vanishes, the coefficient of U must also vanish; so that we must have either $f'_\alpha(U_{-1}) = 0$, which reduces this case to case (I.) already discussed, or we must have $m_1 = m_2$ or $\dfrac{du}{dx} = 0$, a particular case which may be passed over for the present.

We may confine our attention, therefore, to the case where f is linear with respect to U, *i. e.* where

$$f(xyz\mathrm{U}) = f_\beta(xyz) \mathrm{U} + f_\gamma(xyz),$$

where f_β, f_γ do not contain U, but may involve lower derivatives of ϕ. Substituting this value in the foregoing equation, and equating to zero, the coefficient of U in the result, we shall have simultaneously

$$\left. \begin{aligned} 0 &= m_2 f'_\alpha(y) - f'_\alpha(x) - f_\alpha . f'_\alpha(z) - \alpha f_\alpha - \gamma z - \delta \\ &\quad + (m_2 - m_1) \{ f'_\alpha(z) - \mu \} f_\gamma, \\ 0 &= \frac{du}{dy} f'_\alpha(U_{-1}) + \{ f'_\alpha(z) - \mu \} f_\beta, \end{aligned} \right\} \quad . \quad (13)$$

where

$$\mu = \frac{1}{m_2 - m_1} \left\{ m_1 \alpha + \beta + \frac{dm_1}{dx} - m_2 \frac{dm_1}{dy} \right\}.$$

Moreover, substituting in (8^{ii})* the following values of f_x, f_y,

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* It is to be observed that although terms in f_β, f_γ, involving U_{-1}, would give rise to terms in f_x, f_y, involving U, yet those would disappear when we substitute for f_x, f_y in (8^{ii}). Hence in effecting such substitution we need not advert to the fact of whether f_β, f_γ do or do not involve U_{-1}.

f_{ay}, viz.

$$f_x = f'(x) + f'(z)\,\mathrm{F} = f'(x) + f'(z)\,(m_1 f + f_a)$$
$$= f_\beta \cdot \frac{d\mathrm{U}}{du} \cdot \frac{du}{dx} + \overline{f'_\beta(x) + f'_\beta(z)\,(m_1 f + f_a)} \cdot \mathrm{U}$$
$$+ f'_\gamma(x) + f'_\gamma(z)\,(m_1 f + f_a),$$
$$f_y = f_\beta \cdot \frac{d\mathrm{U}}{du} \cdot \frac{du}{dy} + \overline{f'_\beta(y) + f'_\beta(z) \cdot f} \cdot \mathrm{U}$$
$$+ f'_\gamma(x) + f'_\gamma(z) \cdot f,$$
$$f_{ay} = f'_a(y) + f'_a(z) \cdot (f_\beta \cdot \mathrm{U} + f_\gamma) + f'_a(\mathrm{U}_{-1}) \cdot \mathrm{U} \cdot \frac{du}{dy},$$

and equating to zero the coefficient of U in the result, we shall have simultaneously

$$0 = m_1 f'_\gamma(y) - f'_\gamma(x) - f_a \cdot f'_\gamma(z) + f'_a(y) + f_\gamma \cdot f'_a(z) + f_\gamma \cdot \frac{dm_1}{dy},$$

$$0 = m_1 f'_\beta(y) - f'_\beta(y) - f_a \cdot f'_\beta(z) + f_\beta \cdot f'_a(z) + \frac{du}{dy} f'_a(\mathrm{U}_{-1}) + f_\beta \cdot \frac{dm_1}{dy}.$$

Eliminating $f'_a(\mathrm{U}_{-1})$ by means of (13$^{\text{ii}}$), the two last equations may be written

$$\left. \begin{aligned} 0 &= m_1 f'_\gamma(y) - f'_\gamma(x) - f_a \cdot f'_\gamma(z) + f'_a(z) + \overline{\frac{dm_1}{dy}} \cdot f_\gamma + f'_a(y), \\ 0 &= m_1 f'_\beta(y) - f'_\beta(x) - f_a \cdot f'_\beta(z) + \left(\mu + \frac{dm_1}{dy}\right) \cdot f_\beta. \end{aligned} \right\} \quad (14)$$

From (13) and (14) we have to determine f_a, f_β, f_γ.

From what has immediately preceded, it will be evident that the forms of (13) and (14) will be precisely the same, whether f_β, f_γ contain ϕ or any of its derivatives or not. Hence we may assume that f_β, f_γ contain neither ϕ nor its derivatives.

But if f_β do not contain U_{-1}, since f_a contains U_{-1}, and m_1, μ are definite functions of x and y, (14$^{\text{ii}}$) shows that we must have $f'_\beta(z) = 0$. Hence we have for the determination of f_β,

$$0 = m_1 f'_\beta(y) - f'_\beta(x) + \left(\mu + \frac{dm_1}{dy}\right) f_\beta. \quad \quad \quad \quad (14a)$$

Moreover, integrating (13$^{\text{ii}}$), the auxiliary equations for which are
$$0 = d \cdot f_a - \mu dz, \quad \quad dx = 0,$$
$$0 = \frac{du}{dy} dz - f_\beta d \cdot \mathrm{U}_{-1}, \quad dy = 0,$$

whence we have
$$\mathrm{C}_i = f_a - \mu z, \quad \mathrm{C}_{ii} = \frac{du}{dy} z - f \cdot \mathrm{U}_{-1},$$

we get
$$f_a = \mu z + f_1(xy\omega), \quad \quad \quad \quad \quad \quad (15)$$

where

$$\omega = \frac{du}{dy}z - f_\beta \cdot \mathrm{U}_{-1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Substituting the above value of f_α in (13¹), and eliminating U_{-1} from the result by means of (16), we shall get f_γ of the form

$$f_\gamma = \mathrm{C}z + \mathrm{D},$$

where CD are functions of $xy\omega$ only. But as f_γ does not contain U_{-1}, neither can it contain ω; hence we must have

$$\frac{df_\gamma}{d\omega} = 0,$$

and therefore

$$\frac{d\mathrm{C}}{d\omega} = \frac{d\mathrm{D}}{d\omega} = 0.$$

It will be found that

$$\mathrm{C} = \frac{g}{f_1'(\omega)} + h,$$

where h involves x and y only, and

$$g = \frac{1}{(m_1 - m_2)\frac{du}{dy}} \left\{ m_2\frac{d\mu}{dy} - \frac{d\mu}{dx} - \mu \cdot \overline{\mu + \alpha} - \gamma \right\}.$$

Hence

$$\frac{d\mathrm{C}}{d\omega} = -\frac{g}{|f_1'(\omega)|^2} \cdot f_1''(\omega^2).$$

Therefore either we must have $g=0$, which, as has already been pointed out, is the criterion of the given equations being derivable from a single partial differential equation of the first order; or we must have $f_1''(\omega)=0$, from which it follows that f_1 must be linear with respect to ω, so that we may take

$$f_\alpha = \mu z + f_{\beta_1}\left\{ \frac{1}{f_\beta} \cdot \frac{du}{dy} \cdot z - \mathrm{U}_{-1} \right\} + \mathrm{A},$$

$$= \mathrm{A} + (\mu + \epsilon f_{\beta_1})z - f_{\beta_1} \cdot \mathrm{U}_{-1}, \quad . \quad . \quad . \quad (17)$$

where $\epsilon = \frac{1}{f_\beta} \cdot \frac{du}{dy}$, and f_{β_1} and A are functions of x and y which

do not involve U_{-1} or higher derivatives of ϕ, but may involve lower derivatives of ϕ.

(17) gives us, observing that $f_\alpha = f_\alpha(xyz\mathrm{U}_{-1})$,

$$f'_\alpha(x) = \frac{d\mathrm{A}}{d\mu} + \frac{d}{d\mu}(\mu + \epsilon f_{\beta_1})z - f'_{\beta_1}(x) \cdot \mathrm{U}_{-1},$$

$$f'_\alpha(y) = \frac{d\mathrm{A}}{dy} + \frac{d}{dy}(\mu + \epsilon f_{\beta_1})z - f'_{\beta_1}(y) \cdot \mathrm{U}_{-1},$$

$$f'_\alpha(z) = \qquad \mu + \epsilon f_{\beta_1}.$$

Q 2

Substituting these values in (13^i), and equating to zero the coefficient of U_{-1} in the result, we get

$$0 = m_2\frac{dA}{dy} - \frac{dA}{dx} - (\alpha + \mu + \epsilon f_{\beta_1})A - \delta + (m_2 - m_1)\epsilon f_{\beta_1} \cdot f_\gamma$$

$$+ \left\{ m_2\frac{d}{dy}(\mu + \epsilon f_{\beta_1}) - \frac{d}{dx}(\mu + \epsilon f_{\beta_1}) - (\alpha + \mu + \epsilon f_{\beta_1})(\mu + \epsilon f_{\beta_1}) - \gamma \right\} \cdot z,$$

$$0 = m_2 f'_{\beta_1}(y) - f'_{\beta_1}(x) + (\alpha + \mu + \epsilon f_{\beta_1})f_{\beta_1}, \quad \cdots \quad (18)$$

it being assumed for the present that f_{β_1} and A do not contain U_{-2}.

The last equation enables us to determine f_{β_1}. Putting in the preceding one $Cz + D$ for f_γ, where C and D are functions of x and y, which we are entitled to assume do not contain ϕ or its derivatives, and equating to zero the coefficient of z in the result, we have

$$0 = m_2\frac{dA}{dy} - \frac{dA}{d\mu} - (\alpha + \mu + \epsilon f_{\beta_1})A - \delta + (m_2 - m_1)\epsilon f_{\beta_1} \cdot D, \quad \cdot \quad (19)$$

$$0 = m_2\frac{d}{dy}(\mu + \epsilon f_{\beta_1}) - \frac{d}{d\mu}(\mu + \epsilon f_{\beta_1}) - (\alpha + \mu + \epsilon f_{\beta_1})(\mu + \epsilon f_{\beta_1}) - \gamma$$
$$+ (m_2 - m_1)\epsilon f_{\beta_1} \cdot C, \quad \cdots \quad (20)$$

the last of which determines C.

Again, observing that

$$f'_\gamma(y) = \frac{dC}{dy}z + \frac{dD}{dy},$$

$$f'_\gamma(x) = \frac{dC}{dx}z + \frac{dD}{dx},$$

$$f'_\gamma(z) = C,$$

substituting these values with the above values of $f_\alpha, f'_\alpha(z), f'_\alpha(y)$ in (14^i), we get the three following equations, viz.

$$0 = m_1\frac{dD}{dy} - \frac{dD}{dx} + \left(\mu + \epsilon f_{\beta_1} + \frac{dm_1}{dy}\right)D + \frac{dA}{dx} - AC, \quad \cdots \quad (21)$$

$$0 = m_1\frac{dC}{dy} - \frac{dC}{dx} + \frac{dm_1}{dy}C + \frac{d}{dx}(\mu + \epsilon f_{\beta_1}), \quad \cdots \cdots \quad (22)$$

$$0 = f_{\beta_1} \cdot C - f_{\beta'_1}(y). \quad \cdots \cdots \cdots \quad (23)$$

Eliminating C between (20) and the two last equations, we shall have *two* equations of condition to be satisfied by the coefficients of the given equation.

Hence, observing that when $\delta = 0$, (19) and (21) are satisfied by $A = D = 0$, when the coefficients of the given equation satisfy the conditions above indicated, the equation will be capable of being

derived from an integral equation such as to give rise to the following values of p and q, viz. :—

$$p = m_1 f_\beta \cdot U - f_{\beta_1} \cdot U_{-1} + (m_1 C + \mu + \varepsilon f_{\beta_1}) z,$$
$$q = \quad f_\beta \cdot U + C z,$$

where f_β, f_{β_1}, and C are determined as above indicated.

The foregoing result depends upon the assumption that f_{β_1} and A do not contain U_{-2}. Let us now assume, on the contrary, that these functions contain U_{-2}.

If we had

$$f_{\beta_1} = f_b(xy U_{-2}),$$

we should have

$$f'_{\beta_1}(x) = f'_b(x) + f'_b(U_{-2}) U_{-1} \frac{du}{dx},$$

$$f'_{\beta_1}(y) = f'_b(y) + f'_b(U_{-2}) U_{-1} \frac{du}{dy};$$

and the terms in these derivatives of f_{β_1} which involve U_{-1} would give rise to a term in (13^i) of form

$$-f'_b(U_{-2}) \cdot (U_{-1})^2 \cdot \left(m_2 \frac{du}{dy} - \frac{du}{dx} \right),$$

which must vanish,—thus implying either that $f'_b(U_{-2}) = 0$, *i. e.* that f_{β_1} does not contain U_{-2}, or else that

$$m_2 \frac{du}{dy} - \frac{du}{dx} = 0,$$

which last is impossible unless $m_2 = m_1$, a particular case of which we may at present omit the consideration.

But, if A involves U_{-2}, assume

$$A = f \delta(xy U_{-2}),$$

whence we get

$$f'_a(x) = f'_\delta(x) + \frac{d}{dx}(\mu + \varepsilon f_{\beta_1})z - \left\{ f'_{\beta_1}(x) - f'_\delta(U_{-2}) \frac{du}{dx} \right\} \cdot U_{-1},$$

$$f'_a(y) = f'_\delta(y) + \frac{d}{dy}(\mu + \varepsilon f_{\beta_1})z - \left\{ f'_{\beta_1}(y) - f'_\delta(U_{-2}) \frac{du}{dy} \right\} \cdot U_{-1},$$

$$f'_a(z) = \quad \mu + \varepsilon f_{\beta_1};$$

and substituting these in (13^i), we shall get, equating to zero the coefficient of U_{-1}, in the result,

$$0 = -\left(m_2 \frac{du}{dy} - \frac{du}{dx} \right) f'_\delta(U_{-2}) + m_2 f'_{\beta_1}(y) - f'_{\beta_1}(x) + (\alpha + \mu + \varepsilon f_{\beta_1}) f_{\beta_1},$$

whence it is clear that we may put

$$A = A_1 + f_{\beta_2} \cdot U_{-2},$$

where A_1, f_{β_2} are functions of xy, which do not contain U_{-2} or higher derivatives of φ;

$$\therefore f_a = A_1 + \overline{\mu + \varepsilon} f_{\beta_1} \cdot z - f_{\beta_1} \cdot U_{-2} + f_{\beta_2} U_{-2},$$

$$f'_a(x) = \frac{dA_1}{dx} + \frac{d_1}{dx} \overline{\mu + \varepsilon} f_{\beta_1} \cdot z - \left\{ f'_{\beta_1}(x) - f_{\beta_2} \cdot \frac{du}{dx} \right\} U_{-1} + f'_{\beta_2}(x) \cdot U_{-2},$$

$$f_a(y) = \frac{dA_1}{dy} + \frac{d}{dy} \overline{\mu + \varepsilon} f_{\beta_1} \cdot z - \left\{ f'_{\beta_1}(y) - f_{\beta_2} \cdot \frac{du}{dy} \right\} U_{-1} + f'_{\beta_2}(y) \cdot U_{-2},$$

$$f'_a(z) = \qquad \mu + \varepsilon f_{\beta_1}.$$

Substituting these values in (13^i), also putting $Cz + D$ for f_γ, and equating to zero the coefficients of z, U_{-1} and U_{-2} in the result, which last we may do *on the assumption that* A_1 *does not contain* U_{-3}, we shall get the four following equations, viz :—

$$0 = m_2 \frac{dA_1}{dy} - \frac{dA_1}{dx} - (\alpha + \mu + \varepsilon f_{\beta_1}) A_1 - \delta + \overline{m_2 - m_1} \cdot D,$$

$$0 = m_2 \frac{d}{dy} (\mu + \varepsilon f_{\beta_1}) - \frac{d}{dx} (\mu + \varepsilon f_{\beta_1}) - (\alpha + \mu + \varepsilon f_{\beta_1})(\mu + \varepsilon f_{\beta_1}) - \gamma$$
$$+ \overline{m_2 - m_1} \cdot \varepsilon f_{\beta_1} \cdot C,$$

$$0 = m_2 f'_{\beta_1}(y) - f'_{\beta_1}(x) - \left(m_2 \frac{du}{dy} - \frac{du}{dx} - \alpha + \mu + \varepsilon f_{\beta_1} \right) f_{\beta_2},$$

$$0 = m_2 f'_{\beta_2}(y) - f'_{\beta_2}(x) - (\alpha + \mu + \varepsilon f_{\beta_1}) \beta_2.$$

Also, treating in the same manner (14^i), we get

$$0 = m_1 \frac{dD}{dy} - \frac{dD}{dx} - \left(\mu + \varepsilon f_{\beta_1} + \frac{dm_1}{dy} \right) D - CA_1 + \frac{dA_1}{dy},$$

$$0 = m_1 \frac{dC}{dy} - \frac{dC}{dx} + \frac{dm_1}{dy} C + \frac{d}{dy} (\mu + \varepsilon f_{\beta_1}),$$

$$0 = Cf_{\beta_1} - f_{\beta_1}'(y) + f_{\beta_2} \frac{du}{dy},$$

$$0 = Cf_{\beta_2} - f_{\beta_2}'(y).$$

Of these *eight* equations, two may be disposed of by putting $A = D = 0$, having also $\delta = 0$.

By properly combining the remaining six we shall get a partial differential equation of the first order by which f_{β_1} may be determined, and so obtain values for the remaining disposable quantities f_{β_2} and C, there being left a residuum of *three* equations of condition to be satisfied by the coefficients of the given equation.

Hence, when the equation

$$0 = \mathrm{R}r + \mathrm{S}s + \mathrm{T}t + \mathrm{R}(\alpha p + \beta q + \gamma z) \quad . \quad . \quad . \quad (24)$$

admits of being derived from a single integral involving one or more arbitrary functions, and in which the number of the derivatives of one of those functions is not infinite, then, except in certain particular cases presently to be adverted to, in which the foregoing method requires modification, (24) will either be derivable from a single partial differential equation of the first order, in order to which at least one equation of condition must be satisfied by R, S, &c., or else p and q must be capable of assuming the form

$$p = m_1 f + f_\alpha, \quad q = f,$$

where

$$f = \mathrm{C}z + f_\beta \cdot \phi^{(m)},$$
$$f_\alpha = az + a_1\phi' + a_2\phi'' + \&c. + a_{m-1}\phi^{(m-1)};$$

$a, a_1, a_2 \ldots, a_{m-1}$, C, f_β being functions of xy only, m_1 being one of the roots of

$$0 = \mathrm{R}m^2 + \mathrm{S}m + \mathrm{T},$$

and the u of $\phi(u)$ is determined by

$$0 = \frac{du}{dx} - m_1 \frac{du}{dy},$$

—*these results being dependent, however, upon the fact of the coefficients* R, *&c. satisfying as many equations of condition as there are derivatives of* ϕ *occurring in* f *and* f_α.

We have f_β determined by the equation (14a); and the remaining indeterminate quantities C, a_1, a_2, &c. are given by the foregoing theory, although practically, their values, as well as the forms of the equations of condition, will probably be most satisfactorily obtained by assuming, as it is evident we may do,

$$\mathrm{A}z = \phi(u) + \mathrm{A}_1\phi'(u) + \mathrm{A}_2\phi''(u) + \&c. + \mathrm{A}_{m-1}\phi^{(m-1)}(u),$$

in which case it immediately follows, from comparison of the value of p obtained from this equation with that above given, that we shall have

$$\mathrm{C} = -\frac{1}{\mathrm{A}}\frac{d\mathrm{A}}{dy},$$

$$0 = \frac{du}{dy} + \frac{d\mathrm{A}_1}{dy},$$

$$0 = \mathrm{A}_1\frac{du}{dy} + \frac{d\mathrm{A}_2}{dy},$$

$$0 = \mathrm{A}_2\frac{du}{dy} + \frac{d\mathrm{A}_3}{dy},$$

&c. &c.

$$0 = A_{m-2}\frac{du}{dy} + \frac{dA_{m-1}}{dy},$$

$$f_\beta = A_{m-1}\frac{du}{dy}.$$

If the values of m_1, m_2 are constant, I gather that the integral in the cases where it occurs will be of the form

$$Az = \phi(u) = f_\beta^{(m-1)}(y)\phi'(u) \mp f_\beta^{(m-2)}(y)\phi''(u) \pm \&c.$$
$$-f_\beta'(y)\phi^{(m-2)}(u) + f_\beta\phi^{(m-1)}(u),$$

in which it may be conjectured that the number of terms in the series of derivatives of ϕ will in general be defined by the fact of the derivatives of f_β beyond a certain number taking the value zero.

To return to the cases in which the foregoing process requires modification, one of which, it has been already shown, occurs when u contains x or y only.

Suppose u to contain y only, and that

$$p = F(xyzU_{-1}),$$
$$q = f(xyzU_{-1}U),$$

where, as before, U_{-1} or $\phi^{(m-1)}$ is the highest derivative of ϕ in the integral equation. Then

$$\frac{dp}{dx} = F_x + F'(U_{-1}) \cdot 0 = F_x,$$

$$\frac{dp}{dy} = F_y + F'(U_{-1}) \cdot U,$$

$$\frac{dq}{dx} = f_x + f'(U_{-1}) \cdot U \cdot 0 + f'(U) \cdot U_{+1} \cdot 0 = f_x,$$

$$\frac{dq}{dy} = f_x + f'(U_{-1}) \cdot U + f'(U) \cdot U_{+1}.$$

Substitute in the equations (5a) these values, observing that since U_{+1} occurs in $\frac{dq}{dy}$ we must have $T_1 = 0$, and we get

$$0 = R_1 F_x + S_1 F_y + V_1,$$
$$0 = f_x - F_y - F'(U_{-1}) \cdot U.$$

Assume $V = Pp + Qq + Nz + M$, and that R, S, P, Q, N, M are functions of xy only. The last equations become, if we assume $F'(U_{-1}) = 0$,

$$0 = R\{F'(x) + F'(z)F\} + S\{F'(y) + F'(z)f\} \atop + PF + Qf + Nz + M, \quad . \quad . \quad . \quad . \Big\} \quad . \quad (25)$$

$$0 = f'(x) + f'(z)F - F'(y) - F'(z)f. \quad . \quad . \quad . \quad (26)$$

Since f contains U and F does not, (25) gives us

$$0 = RF'(x) + SF'(y) + R \cdot F \cdot F'(z) + PF + Nz + M, \quad (27)$$

$$0 = S \cdot F'(z) + Q.$$

The last gives us

$$F'(z) = -\frac{Q}{S},$$

$$\therefore F = -\frac{Q}{S}z + F_a(xy);$$

and

$$F'(x) = -\frac{d}{dx}\left(\frac{Q}{S}\right)z + F_a'(x),$$

$$F'(y) = -\frac{d}{dy}\left(\frac{Q}{S}\right)z + F_a'(y).$$

Substituting these values in (27) and putting the coefficient of z in the result $= 0$, we get

$$0 = RF_a'(x) + SF_a'(y) + \left(P - Q\frac{R}{S}\right)F_a + M, \quad . \quad . \quad (28)$$

$$0 = R\frac{d}{dx}\left(\frac{Q}{S}\right) + S\frac{d}{dy}\left(\frac{Q}{S}\right) + \left(P - Q\frac{R}{S}\right)\cdot\frac{Q}{S} + N,$$

the last of which equations was shown in my previous paper to be the condition to be satisfied by the coefficients, in order that the given equation may be derivable from a single equation of the first order into which p does not enter; while (28) affords the means of ascertaining such single equation.

F being determined, (26) gives us the value of f which will contain an arbitrary function of y.

If F be supposed to contain U_{-1}, we must go through much the same process as is above adopted in the general case when the integral takes the form of a series of derivatives of ϕ; the details I here omit.

A reference to (6) will show that the results derived from those equations in the earlier part of this paper fail when R or T vanishes. I believe that these cases of failure, however, will be found to resolve themselves into that which has already been discussed.

With regard to the general tenor of the results of this and of my previous paper, I offer the following remarks.

A partial differential equation of the second order between *xyz* may always be replaced by two partial differential equations of the first order between x, y, z, p, q (see 5a). That such a pair of equations should be derivable from a single equation between x, y, z, p, q is obviously what cannot generally occur; *i.e.* its occur-

rence requires that at least one equation of condition shall be satisfied, as is shown in my previous paper.

On the other hand, when an equation of the second order between x, y, z is derivable from an integral equation involving even a single arbitrary function, it is clear from what has herein appeared that the given equation may be replaced by a pair of equations between x, y, z, p, q and their differential coefficients of the first order, which pair will be derivable from a pair of integral equations between x, y, z, p, q involving at least one arbitrary function. The occurrence of this arbitrary function will, as has been seen, split each of the equations to be satisfied, viz. (5a), into two, thus giving us four in all, while we have but three disposable quantities, viz. F, f, u, wherewith to satisfy them— a circumstance from which it follows inevitably that the occurrence of integrals of the kind treated of in this paper must be conditional.

At the same time, nothing has herein appeared which shows, nor am I aware of any argument which tends to show, that a partial differential equation of the second order between x, y, z will not always be satisfied by a single integral equation free from arbitrary functions.

6 New Square, Lincoln's Inn,
    February 22, 1868.

XXV. *On the Sounds produced by a Jet of Water.*
    By C Sondhauss[*].

IN some posthumous papers of F. Savart there is an investigation of the sounds which are formed when water issues from short tubes placed in vessels. The sounds were most easily produced when the height of such tubes or apertures was equal to their diameters; and Savart found in this case that the number of vibrations of the notes which belong to the same scale was as the square roots of the pressures of water, and inversely as the heights of the tubes. Where the apertures had other dimensions, owing to the difficulty of determining the note no more could be said than that, with equal pressures, the ratio of the numbers of vibrations did not seem greatly to differ from the inverse ratio of the lengths of the tubes.

When the water issued into air, a note was only obtained in case the height of the aperture was between half and double the diameter; when the water flowed into water, a tone resulted if the height of the aperture amounted to $\frac{1}{10}$ the diameter.

Almost simultaneously M. Sondhauss made an extended in-

* From an abstract in the *Fortschritte der Physik*, vol. xxi. by Dr. Röber, of the original paper which formed part of the " Programme der Real-Schule zu Neisse," Poggendorff's *Annalen*, vol. cxxiv. p. 1.

vestigation "On the notes formed by a jet of air." A current of
air issuing from an aperture in a thin plate gave no independent
note, but began to sound when a suitable note (according to the
data the number of vibrations appears proportional to the velocity
of efflux) was sounded in the vicinity. But an independent note
was produced if, at some little distance above the aperture, a
plate was held with an aperture of about the same size; and the
result was obtained that the number of vibrations of the note
was directly as the velocity with which the air issued, and
inversely as the distance of the plate. The notes are formed even
with as low a pressure as 55 millims., if the plate is more than
1 millim. from the aperture. It may be shown, by means of
tobacco-smoke, that the emergent current only forms a continuous
column for about an inch from the aperture; and M. Sondhauss
thinks that this column of air acts like a solid rod, which by
friction against the edges of the two apertures forms sonorous
vibrations. Apertures in a thick plate, at the end of wide cy-
lindrical tubes, gave notes which were influenced by the note of
the tube.

M. Sondhauss has made analogous experiments on the pores
of a water-jet.

A closed iron-plate cylinder A, 3 inches in diameter, and 3½
in height, had a circular aperture at the top, over which plates
and other apparatus could be suitably fixed. This could be fed
with water from a reservoir, at a height of 4 feet, by means of an
indiarubber tube provided with a Bunsen's clamp. In order that
water might issue either into air or into water, the wall of the
cylinders was prolonged to a height of 2½ inches above the top,
so as to form a sort of cistern; and in order to regulate the
height of the water in this, there was a tubulure in its side,
just above the top of the cylinder, in which was fitted, by
means of a cork, a glass tube bent twice at right angles, which
could thus be easily raised or lowered. With the interior
of the vessel a manometer was connected for measuring the
pressure of the water, the supply of which from the reservoir
could be regulated by means of the clamp. The vessel was also
provided with a vertical scale, the vernier of which was furnished
with a bent rod, on which could be fixed the plates with different-
sized apertures which were to be held against the jet.

Besides this cylinder, a larger vessel, B, was used, consisting
of an upright wine-cask; in an aperture on the top of this a
cylinder open at the bottom could be fitted. The water was
supplied from the higher reservoir through the bung-hole, by
means of a caoutchouc tube with a clamp.

When the water flows, under a small pressure, from an
aperture in the top of the cylinder, a small elevation only is

produced in the middle of the water-surface, while the surface is otherwise at rest; with greater pressures of 2 to 3 feet rapid undulations are formed. No sound, however, is produced. If, however, a knife or edge of any kind be held in the jet at a distance of a few millimetres from where it emerges, tones are formed which are analogous to those of the current of air; they are most certainly and most distinctly produced if a plate with an aperture corresponding to that of the jet be held over the jet.

The apertures were mostly circular, yet four- or three-sided apertures were also used. Large apertures require too great a quantity of water, and the quantities of water which pass through the upper aperture are liable to produce disturbing vibrations. The best results were obtained with circular apertures 2 millms. in diameter, which were therefore generally used for the sake of comparison; apertures of 3·5 millims. and 5 millims. were also used.

As the pressure of water increases, the tone is in general higher and stronger; but after it has been under this condition for some time, it will suddenly become feebler, yet starts again more powerfully when the pressure increases; or it is quite silent, and can only be again worked by a further definite increase of pressure; or all at once it will become deeper by a definite interval, for instance a fourth, again attaining the same height or a greater one as the pressure increases. If the pressure decreases, the same phenomena occur in the inverse order, but with this difference, that notes once formed continue for the most part, even with a somewhat smaller pressure than that at which they first occurred during the increase of pressure. With a definite pressure of water some tones are formed particularly pure and sonorous; with others, the tones are accompanied by an unpleasant roaring and grating, which often occurs alone. Very often three tones are heard at the same time, of which, when the pressure is changed, one preponderates and is afterwards alone heard. The mixed sounds, consisting of several notes which frequently form no pure interval with each other, greatly increase the difficulty of observing the height of the note, and frequently make the observer distrust his own judgment. It is often particularly difficult to decide to which octave the note perceived belongs.

The note is similarly altered by varying the distance of the plate from the aperture; by increasing the distance it gradually becomes deeper, then suddenly becomes higher, or perhaps entirely disappears, but occurs again at a still greater distance. Even if the two apertures are somewhat different from each other, by a suitable velocity and distance of the plates, the tones may be evoked, though more feebly and to a less extent. With a

circular aperture of 3·5 millims. in diameter, the experiment succeeded even when the aperture of the upper plate was 0·5 millim. smaller or greater. Even when a suitably bent strip of lead was placed on one side of the jet at a proper distance from the aperture, notes were formed which changed with the distance of the strip.

When small apertures were used, the notes produced with the smaller cylindrical apparatus A were more easily obtained, and were richer and more varied as to height and quality; while those produced with the apparatus B fitted on the cask were feebler, but altered more uniformly with the pressure of water and the distance of the plates. More powerful jets also produced more powerful tones in the larger apparatus.

The size and shape of the aperture influences the character of the tone produced; so that with another aperture, other circumstances being the same (that is, the pressure of water and the distance of the upper plate), different notes are in general formed; yet no definite connexion could be ascertained to exist between the dimensions of the apertures and the height and other characters of the note.

If the two plates are cemented together by a cork ring, the whistle thus formed gives more or less distinct and rich notes, which depend upon the velocity of efflux, and are less changeable than those hitherto described.

As compared with the sounds produced by air, those obtained with water are in general lower and feebler, and have smaller compass and variety. The pressure under which the jet of water emerges must be greater, but the distance of the plates smaller than in the case of air. The pressure most suitable for the formation of a sound with a jet of water appeared to be between 5 and 16 inches, while in the earlier experiments on the production of sounds by air a pressure of from 1 to 30 millims. was generally used. The distance of the plates in the former case was about half that which was found suitable in the latter.

The author gives as a law, which holds good for the notes of the jet of water within certain limits, that the number of vibrations of the notes belonging to the same scale are as the square roots of the pressures, or as the velocities, and are inversely as the distance of the upper plate from the aperture. If the velocity of efflux and the distance of the plates be changed, a few notes of definite height become prominent from their rich quality, or pauses result between definite notes. For such a characteristic note or such a pause the ratio of the corresponding velocity of efflux and the distance of the plates is almost constant.

The author communicates three series of his valuable and multifarious experiments. They indicate an increase in the

height of the tone as the velocity of efflux increases, as well as a decrease in the height of the tone with increasing distance of the plate. They do not, however, seem to justify the establishment of the law just laid down.

The author's view as to the origin of the notes is the same as that given in his former experiments on the sounds of the jet of air. He regards " the jet emerging from the aperture as a moving rod which by friction against the edges and angles is set in longitudinal vibrations, just like wooden rods and horsehairs when drawn through the fingers ;" and only that part has to be taken into account which lies between the two rubbed parts. That the jet acts as a special substance differing from the surrounding medium, follows from the circumstance that the notes are not formed merely when the jet issues into water, but also when it flows into air. If the jet ascends in the air without sounding, it is smooth and transparent like a glass rod ; on the contrary, when it sounds, it is rough and opake.

For the experiments on the tones formed when water is driven through apertures in thick plates the larger apparatus B was used. Mere plates, of different thickness, gave no sound, whatever was the velocity with which the jet was driven through them ; yet if the same plates, which to prevent their own oscillations were made of lead, were cemented in tubes, and the pipes thus formed fitted water-tight in the apparatus, the water-tones were produced in sufficient variety. The plate was generally at the top of the tube, a few centimetres below the level of the water ; yet with cylindrical or prismatic apertures the same notes were in general formed, whether the plates were above or below.

The tubes sounding by water sound generally also with air ; yet it also sometimes happens that a tube will only sound with a current of air, or, with a small aperture in a thin plate, with a current of water. The tones with water are, generally speaking, deeper and poorer than the air-tones. With increasing pressure the air-tones frequently pass over to two or three, or frequently more, harmonics, while the water-notes seldom make sudden leaps with increasing pressure, but gradually become higher. The greater steadiness of the water-notes may have its origin in the particular length of the tubes used by the author, which, as compared with the velocity of sound, is small. If the aperture in the plate is conical, a note is only formed in case the current passes in the direction of the widening of the cone. For water-notes the widening of the cone must not be considerable, while for air-tones this is to a certain extent advantageous.

The results of these investigations agree in general with the laws discovered by Savart.

XXVI. *Proceedings of Learned Societies.*

ROYAL SOCIETY.

[Continued from p. 153.]

January 23, 1868.—Dr. William B. Carpenter, Vice-President, in the Chair.

THE following communication was read :—
" Description of a Hand Spectrum-Telescope." By William Huggins, F.R.S.

The instrument described in this paper was contrived in the summer of 1866, for the purpose of observing the spectra of meteors and their trains. The special suitability of this apparatus, as *a hand-spectroscope*, for the examination of the spectra of the lights which may be seen about the sun during the total solar eclipse of next year, induces me to offer a description of it to the Royal Society.

The apparatus consists essentially of a direct-vision prism placed in front of a small achromatic telescope.

The achromatic object-glass, marked *a*, is 1·2 inch in diameter, and has a focal length of about 10 inches. The eyepiece (*b*) consists of two plano-convex lenses. As a large field of view is of great importance, especially for its use as a meteor-spectroscope, the field-lens is made of nearly the same diameter as the object-glass. The imperfect definition at the margin of the field is not of much practical importance, as the spectra can be brought for examination into the centre of the field. The field-lens is fixed in a sliding tube, which permits the distance between the two lenses of the eyepiece to be altered ; in this way the magnifying-power of the instrument may be varied within certain limits at pleasure. Before the object-glass is fixed a direct-vision prism (*c*), consisting of one prism of dense flint glass, and two prisms of crown glass.

The field of view of my apparatus embraces an area of sky of about 7° in diameter. The spectrum of a bright star has an apparent length of nearly 3°. The spectrum of the Great Nebula in Orion appears as two bright lines, one of them broad, crossed by a faint continuous spectrum. The magnifying-power of the telescope is insufficient to show the three distinct lines of which the spectrum of the nebula consists. The continuous spectrum is due to the stars of the trapezium, and the other fainter stars scattered over the nebula.

For the purpose of testing the efficiency of this instrument as a meteor-spectroscope, I observed the spectra of fireworks seen from a distance of about three miles. The bright lines of the metals contained in the fireworks were seen with great distinctness. I was able to recognize sodium, magnesium, strontium, copper, and some other metals.

Unfortunately I was prevented from making the use of the instrument which I had intended at the display of meteors in November 1866. I have, however, great confidence in the suitability of the apparatus for the prismatic observation of meteors and their trains.

As the instrument is not provided with a slit, it is applicable only to bright objects of small size, or to objects so distant as to subtend but a very small angle. It is obvious that if the object has a diameter smaller in one direction than in any other, as would usually be the case with the trains of meteors, the instrument should be rotated to take advantage of the form of the object. The most favourable position will be when the smallest diameter of the object is perpendicular to the height of the prisms. In this way I have seen the lines of Fraunhofer in the spectrum of the moon when a very narrow crescent.

In the case of objects which appear as points, a small breadth may be given to the spectrum by a cylindrical lens fitted in a little cap which slips over the eye-lens, and is placed next to the eye.

As some of the advantages which this instrument possesses over an ordinary spectroscope, or over a prism held before the eye, may be stated the comparatively large amount of light which the object glass collects, the great facility for instantly pointing the instrument to the object desired, which the large field of view affords, and in some cases the magnifying-power of the instrument.

It may perhaps be mentioned that secret signals might be conveyed at night by means of the temporary introduction of certain suitable substances, as preparations of lithium, copper, strontium, &c., into the flame of a lamp giving a continuous spectrum; the presence of the bright lines due to these substances would not be perceived except by an observer provided with a spectrum-telescope, to whom they might convey information in accordance with a previous arrangement.

This little instrument, held in the hand and directed to the place of the sun during its eclipse in 1868, might enable an observer, who was not provided with larger apparatus, to give an answer to the important question whether the bright prominences are self-luminous or reflect solar light. At least it would be possible for him to determine the general character of the spectrum of a bright prominence so far as to learn whether it is continuous or consists of bright lines. On account of the low magnifying-power of the instrument, the red prominence would appear sufficiently small to permit of bright lines being distinguished on its spectrum, if such should exist.

The instrument should be previously focused by the observer on the moon, or some distant object.

Should a portion of the sun's limb be visible, the instrument must be rotated until the spectrum of the little projecting prominence appears in a direction parallel to that of the spectrum of the sun's limb, and is not overlapped by it. Perhaps a diaphragm across the field of view and cutting off about one-third of it would be an advantage, as the spectrum of the sun's limb might be concealed behind

it. The eye, relieved in this way from the bright solar spectrum, would be in a more favourable state to examine the fainter spectrum of the red prominence.

Four of these instruments, made by Mr. Browning, have been sent out by the Royal Society to India, to be placed in the hands of observers stationed at different places along the central line of the eclipse. This instrument would be specially suitable for use at sea.

Postscript.—Mr. Browning has recently suggested a method of diminishing the apparent velocity of meteors by the use of a concave cylindrical lens placed with its axis perpendicular to the direction of their motion. This mode of observing may be applied to the spectrum-telescope by substituting, when required, a plano-convex cylindrical lens for the eye-lens of the eyepiece. If this lens be placed with its axis parallel to the height of the compound prism before the object-glass, and if the telescope be held in a position such that the direction in which the light of the meteor is dispersed is perpendicular to that of its motion, the spectrum of the meteor will be magnified, as when the ordinary eye-lens is employed, but the apparent velocity of the meteor will be less by an amount equal to the magnifying-power of the eye-lens.

XXVII. *Intelligence and Miscellaneous Articles.*

ON STELLAR SPECTRA. BY FATHER SECCHI.

I BEG to offer a continuation of my last communication on stellar spectra (Phil. Mag. vol. xxxv. p. 78). In continuing these investigations I was led to examine the red stars in order to ascertain whether my supposition as to the nature of their spectra was justified.

A good catalogue of these stars is found in the *Connaissance des Temps,* vol. xv., drawn up by Lalande ; and there is a more extensive and complete one in the *Astronomische Nachrichten,* No.1591. I have examined a great number of those now visible, down to the 8th magnitude. This limit is necessary, owing to the direct light of the sky, which gives so much brightness in the field that the light of the smallest stars spread by dispersion is no longer recognizable. It is seen merely in the case of the nebulæ, which only exhibit a very small dispersion for some rays. There is thus probably an absolute limit, even with a more powerful lens than one of nine inches.

The conclusions at which I have arrived are as follows :—

I. The red stars have generally spectra of the third type (like α Orion, α Herculis, β Pegasi, Antares, o Ceti ; when the colour is pale, they might be referred to one intermediate to the second and third.

II. The spectra of a great number of these stars of the 5th or 6th magnitude are perfectly resolvable into bands, which again can be resolved into lines more or less spread out. Such are the following :—

Right ascension.	Declination.	Magnitude.
h m s	° ′	
$\alpha = $ 5 24 1	$\delta = +$ 18 29	5·5
4 46 5	+ 2 16	5·5
4 44 37	+ 14 1	5
22 59 57	+ 8 39	5·5
23 11 6	+ 48 15	

There are a great number of others which cannot be resolved into secondary lines, owing to their feebleness, but the principal lines of which are sufficient to indicate the type.

III. The stars which are not referable to the three types established elsewhere are very rare. I have examined, without success, several hundreds of small stars below the 7th magnitude. I have met with one very extraordinary one ; it is comprised in Lalande's catalogue ($\alpha = 4^h$ 54^m 10^s, $\delta = +0°$ 59′). Its spectrum is very curious : the red is divided into two bands by one large dark line, the golden yellow is reduced to a very clear and very bright line ; after a large dark band follows a large dark-greenish-yellow band, and then, after another dark space, a third zone. I imagine that this spectrum is only an exaggeration of the third type ; I have at present no exact measurements, the instrument being only arranged at present for preliminary observations.

Although I have not yet examined the entire heavens, I think it pretty probable that but few of these stars will be found, and that they will be of the family of the red and of the variable stars.

Sirius, which is very high just now at a convenient time, has been examined by the new spectroscope with a cylindrical eyepiece ; the beautiful dark line in the extreme red is seen sharp and precise, like the line F, and like those of the violet. This just confirms what I saw at the outset, when I only used the prism with the telescope without any eyepiece. Between this and the line D of sodium, which is easily seen in the spectrum of Sirius, a band tolerably spread out is seen nebulous and badly defined, and several other fine lines in the green, already noticed by Mr. Huggins.

I hope soon to be able to give exact measurements for these lines ; but a general review of the heavens must first be made, so as to ascertain the most remarkable stars.—*Comptes Rendus*, January 20, 1868.

ON OXYCHLORIDE OF ZINC AS A CEMENT.   BY DR. TOLLENS.

Soret has, as is well known, used the solid mass resulting from the mixture of chloride and oxide of zinc, more, however, in making small objects than as a cement. It has also been used for stopping teeth.

This cement is admirably adapted for the laboratory ; by its means a vessel may be closed perfectly air-tight in a very durable manner : thus a chlorine wash-bottle was for a quarter of a year in use with-

out needing any repair. To attain this, however, care must be bestowed on its preparation and application.

Commercial zinc-white is mixed with half its volume, or an equal weight, of fine sand, and rubbed in a mortar with solution of chloride of zinc of 1·26, so as to form a homogeneous paste, which is applied as quickly as possible. The weight of the solution required will be about the same as that of the oxide of zinc.

If the solution is of this strength, there is time to apply it to the vessel, and, on setting, it will have an adequate degree of hardness; with a greater degree of concentration, the hardening proceeds too rapidly, while with a less the hardening is insufficient. The cork is pressed a little in the neck of the apparatus, so that there is a hollow space of 2 to 3 lines about the glass tube; after moistening this with the solution, it is filled up with cement, which is laid on a little round the tube. Owing to the rapid hardening of the oxychloride, the apparatus can be used a few minutes after.

In disengaging chlorine, there is scarcely any annoyance from the gas, so that a change of workmen is not necessary, as was formerly the case.

It may be used for many other purposes—cementing glass lutes in metal tubes, closing slits in metal apparatus, &c.

The cost is not great; with less than an ounce of zinc-white, and the same quantity of sand and of solution, a pretty large washbottle may be made tight.—*Zeitschrift für Chemie*, September 1867.

EXPERIMENTS ON THE PERMEABILITY OF CAST IRON BY THE GASES OF COMBUSTION. BY MM. H. SAINTE-CLAIRE DEVILLE AND TROOST.

General Morin has done us the honour of calling for an exact analysis of the air which circulates round a strongly heated cast-iron stove. We have found that this air contained considerable quantities of hydrogen and of carbonic oxide. This fact is completely explained by the permeability to gases of cast iron at a high temperature, and by its property of condensing carbonic oxide discovered by Mr. Graham. It shows, moreover, that the air which is in contact with strongly heated iron surfaces may become injurious to respiration.

We proposed to ascertain whether the porosity of cast iron would allow the gases of combustion to pass through the sides of cast-iron stoves and to diffuse into the atmosphere of heated rooms.

The principal part of the apparatus we used was a cast-iron stove, resembling in shape those used in guard-rooms, and consisting of a cylinder communicating with the exterior by two apertures, by one of which air enters under the grate, while the other, which is in the upper part, terminates in the stove-pipe. By the latter aperture is introduced the combustible (coke, coal, or wood), which is received on a grate at a suitable height above the lower aperture.

The stove was raised successively to various temperatures between red heat and bright redness. It is surrounded by a metal envelope

which, resting in grooves on the top and bottom of the stove, forms a chamber round it which is only connected with the external air by the interstices in the grooves between the envelope and the cylinder.

To investigate the nature of the gases which might pass from the stove proper into the room, the following arrangements were adopted. The gases which transpire into this chamber are aspired into a meter placed at the end of a series of absorption-tubes; they deposit their carbonic acid and aqueous vapour in U-tubes, some filled with pumice soaked with strong sulphuric acid, and some with pieces of potash. Thus purified, they pass over oxide of copper heated to redness; the hydrogen and carbonic oxide they contain are converted into aqueous vapour and carbonic acid. These substances are weighed by being successively passed through tared tubes, the first containing pumice impregnated with concentrated sulphuric acid, and the second potash. The gases are then drawn into the meter, which sends them into the atmosphere.

[It would seem, from an extensive Table furnished by the authors, that 1000 litres of air drawn through the tubes contained, on the average, about $\frac{1}{2}$ a litre of hydrogen and $\frac{1}{2}$ a litre of carbonic oxide. These gases therefore pass through the sides of a cast-iron stove heated to dull or to bright redness.]

These results are readily explained if we remember the porosity of iron, and the greater porosity of cast iron[*].

Graham's experiments have shown, moreover, since our own of 1863, that iron absorbs at a red heat 4·15 times its volume of oxide of carbon when it is exposed to an atmosphere of this gas.

The oxide of carbon absorbed on the inside of the stove diffuses on the outside into the air; and the effect is continuous; hence the disagreeable nature of the air in rooms heated by cast-iron stoves, or by air in contact with red-hot plates.—*Comptes Rendus,* January 13, 1868.

ON CURVES FULFILLING THE EQUATION

$$\frac{d^2\phi}{dx^2} + \frac{d^2\phi}{dy^2} = 0.$$

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

I find that the property of multiple points in curves fulfilling the above condition, demonstrated in a paper which I sent to the Royal Society last year, and which appeared in their 'Proceedings' and in your Magazine, had been previously published a few years ago by M. Haton de la Goupillière in the *Journal de l'École Polytechnique.*

I am, Gentlemen,

Your most obedient Servant,

W. J. MACQUORN RANKINE.

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[*] We have not yet found cast-iron tubes which would preserve a vacuum.

XXVIII. *On certain Cobaltamines.*
By EDMUND J. MILLS, *D.Sc., F.C.S.**

HAVING had occasion in the course of my work to prepare cobaltic hexammoniotrichloride in considerable quantity, I have been led to perform some experiments with that substance and the two pentammoniotrichlorides. The results, I believe, are not without sufficient interest to be recorded in this place.

I. *Cobaltic Hexammoniotrichloride.*

Any one who has employed Gibbs's process for the separation of the metals which are associated in platinum ore must have recognized the extreme value of this compound as a reagent, and the great importance of being able to prepare it with certainty on the large scale. The literature of the subject, unfortunately, supplied only the converse of these two conditions; but the general nature of the reaction whereby the body is usually formed could be perceived without difficulty. When an ammoniacal solution of cobaltic chloride is mixed with sal-ammoniac and exposed to air, the first expenditure of chemical force with which we are here concerned is devoted to the formation of the α-pentammoniotrichloride (roseochloride); on further effort, the β-pentammoniotrichloride (purpureochloride) is produced; and, lastly, the appearance of the hexammoniotrichloride represents the

greatest amount of work performed. That the three chlorides are generated in this order is generally admitted; and I think the above dynamical view of the process will be acknowledged as correct. It is supported, at any rate, by a remarkable result, first obtained by the distinguished American chemist already mentioned. Gibbs found* that the β-disulphate, on treatment with water, splits into the α-sulphate and free hydric sulphate. Work done in decomposition here effects, as might have been foreseen, a return to the point at which the opposite kind of work had been attended with its first consequence.

(1) Cobaltic hexammoniotrichloride is readily obtained when cobaltic chloride is heated with sal-ammoniac and aqueous ammonia in presence of an energetic oxidizing agent. It is best to carry out the operation under pressure; and for this purpose a soda-water bottle with an india-rubber stopper, which can be closed tightly by a simple screw-arrangement, will be found of great convenience. The most suitable temperature of digestion is about 70° C. for a period of not less than twenty hours; and the number of oxidizing agents which may be employed is probably very considerable.

One part (15 grms.) of sal-ammoniac, potassic permanganate, and crystallized cobaltic chloride† respectively, together with $6\frac{1}{4}$ parts of strong aqueous ammonia, yield, after digestion as above mentioned, an orange-coloured liquid and warty aggregates of the desired chloride. There is a copious deposit of manganic, containing cobaltic, peroxide. The ammoniacal liquid is transferred to a beaker containing an excess of aqueous hydric chloride; the crystalline aggregates are dissolved out by hot water containing a little hydric chloride, and their solution is mixed with the preceding; a double volume of strong aqueous hydric chloride is added to the mixture, which is then left to itself for twenty-four hours; at the end of that time the yellow precipitate is removed to a filter and washed, first with aqueous hydric chloride, and finally with spirit. In this manner, about 71 per cent. of the theoretical quantity of the hexammoniochloride is obtained.

(2) If 1 part of potassic dichromate be used instead of the potassic permanganate in the above process, the amount of chloride obtainable corresponds to very nearly 80 per cent. of the calculated yield.

(3) One part of crystallized cobaltic chloride, 1 part of native manganic binoxide ‡ in fine powder, 2 parts of sal-ammoniac, and

* Silliman's American Journal, vol. xxiii. p. 322.
† Vide *infra*.
‡ Since these experiments were performed, Braun has published two processes in which manganic and plumbic peroxide respectively are em-

4·4 parts of aqueous ammonia likewise furnish, under similar treatment, abundance of the hexammoniochloride.

(4) Dicobaltic teroxide is almost wholly transformed into this substance when heated in sealed tubes at 70° with large quantities of sal-ammoniac and strong aqueous ammonia.

(5) The same is true of the hydrous mixture of cobaltic *n*-oxide and silica which is precipitated when cobaltic hexammoniochloride or β-pentammoniochloride is decomposed by about thirty or forty times its weight of water in sealed glass tubes at 70°–100° C.

(6) Even a very weak solution of cobaltic chloride, to which abundance of sal-ammoniac, strong aqueous ammonia, and solid calcic oxychloride have been successively added, will give, after eighteen hours' repose, a decided yellow precipitate with hydric chloride.

(7) A concentrated solution of cobaltic chloride is treated with rather more ordinary aqueous ammonia (previously diluted with its own volume of water) than is necessary to dissolve it; iodine or bromine is next added in small portions at a time, but not so as to saturate the whole of the ammonia; and then, if a considerable bulk of a mixture of equal volumes of spirit and aqueous hydric chloride be stirred in, a crystalline powder falls which is very nearly pure cobaltic hexammoniochloride.

(8) Cobaltic β-pentammoniochloride is converted into hexammoniochloride by digestion at 60°–70° in sealed tubes, with strong aqueous ammonia (of sp. gr. 0·887 at 12°·5), either in the presence or absence of sal-ammoniac. According to Frémy[*], mere ebullition of the chloride and aqueous ammonia will suffice to effect the conversion required. I have verified this statement; but the quantity of product is so excessively small that the process is practically useless. That the generally received equation[†]

$$(\beta)\ 5\,NH^3 . CoCl^3 + NH^3 = 6\,NH^3 . CoCl^3$$
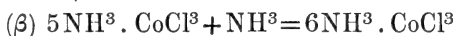
is not true, will be apparent from the following numbers :—

(*a*) 0·4255 grm. pentammoniochloride, dried at 60°–70°, and digested for about eighteen hours, as above specified, yielded, on extraction with dilute aqueous hydric chloride and precipitation with alcohol to which much hydric chloride had been added, a quantity of the hexammoniochloride which, when placed on a

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ployed (*Ann. der Chem. und Pharm.* vol. cxlii. p. 50): the action is allowed to take place in vessels which are open to the air. Judging from the description given by that chemist, the results are very much more satisfactory if the operation be performed as I have suggested, in vessels which are hermetically sealed and subsequently heated.

[*] Pelouze et Frémy, *Traité*, 3rd edit. vol. iii. 1. p. 565.   [†] Co = 60.

filter, washed with strong alcohol, and dried at 40°–70°, amounted to 0·4119 grm.

(*b*) 0·5471 grm. substance, similarly treated (except that the spirit used contained less hydric chloride), gave 0·5168 grm. hexammoniochloride.

(*c*) 0·5626 grm. substance, extracted with warm water and precipitated with spirit only, gave 0·5045 grm. product.

(*d*) 0·5754 grm. pentammoniochloride, 1·8150 grm. sal-ammoniac, and 8 cubic centims. aqueous ammonia, after digestion for twenty-two hours and treatment as in (*c*), gave 0·5852 grm. hexammoniochloride.

	Found.				
	(*a*)	(*b*)	(*c*)	(*d*)	Calculated.
Yield per cent. .	96·80	94·46	89·67	101·70	106·76

In the above experiments the quantity of the chloride produced was ascertained by collecting it on a filter, washing, drying, and weighing; the filter was then thoroughly washed with warm *water*, dried, and again weighed; the difference between these two weights was the number required. In (*c*) and (*d*), the former more especially, there was a residue of cobaltic peroxide on the filter; in (*a*) and (*b*) there was, of course, none of this. It will be observed that extraction with aqueous hydric chloride increases the yield, and that the presence of sal-ammoniac in the digesting mixture has the same effect. The action in both cases is essentially that of chlorine on cobaltic chloride in presence of ammonia. It will also be remarked that the water of the aqueous ammonia is not prevented from producing to a certain extent a decomposition which might be entire were the ammonia absent.

Sal-ammoniac and cobaltic chloride were found in the alcoholic filtrate from (*c*). Further proof that the hexammoniochloride is not a direct result of the combination of ammonia with the β-pentammoniochloride may be found in the fact that the latter chloride, if heated to 87° in a current of dry ammonia for an hour, experiences no increase in weight, whereas when sealed up with strong aqueous ammonia, and submitted to the previous conditions, abundance of hexammoniochloride is formed. As it is known that no greater pressure than that of the atmosphere is absolutely essential to the success of the latter experiment, it follows that the presence of water (in other words, the occurrence of a complex reaction) is necessary for the genesis of the substance in question.

Action of Water on Cobaltic Hexammoniochloride.—According to various authors, the aqueous solution of this chloride is soon decomposed on ebullition; the yellow liquid becomes colourless,

gives off ammonia, and throws down a brown or black precipitate. This precipitate is said by Frémy[*] to consist (if potassic hydrate has been present) of hydrous dicobaltic teroxide; and Gibbs and Genth[†] assign to the product of the action of water on the roseochloride the formula $(Co^3 O^4 . 3 H^2 O)$, whose anomaly they do not leave unnoticed. It is difficult, indeed, to reconcile this,

$$2[6NH^3 . CoCl^3] + (3+n)H^2 O = Co^2 O^3 . nH^2 O$$
$$+ 6(NH^3 . HCl) + 6 NH^3,$$
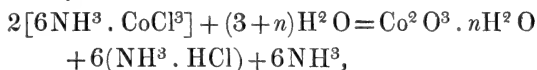
which seems at first sight to be the only probable equation, with the actual results of experiment.

If the action be carried out in sealed tubes at $70°$–$100°$, there are obtained, after several hours, a colourless liquid and a black precipitate. For complete decomposition, the chloride requires from thirty to forty times its weight of water; and the glass tube, whether hard or soft, is very much corroded, often becoming white and opake on cleaning. The black precipitate contains cobaltic peroxide, silica, and water.

0·1661 grm. of the above precipitate, dried over oil of vitriol for a month, was treated with pure hydric sulphate, the liquid evaporated, and the residue gently ignited. Water extracted from this 0·2543 grm. cobaltic sulphate, which was weighed after ignition in a crucible; the insoluble portion consisted of silica, and weighed 0·0226 grm.

0·2018 grm. substance, heated below visible redness in a current of carbonic dioxide, did not change its appearance, and lost 0·0167 grm. water.

The percentage results are as follow :—

	Found.			$Co^4 O^5$.	$Co^3 O^4$.	$Co^2 O^3$.
Cobalt .	58·88	⎫ ⎧ 75·37		75·00	73·77	71·43
Oxygen .	19·24	⎭ ⎩ 24·63		25·00	26·23	28·57
Silica .	13·61					
Water .	8·27					
	100·00	100·00		100·00	100·00	100·00

This result is in apparent disagreement with the numbers obtained by Frémy and Gibbs and Genth; for there does not seem to be any reason why the employment of pressure, of potassic hydrate, or of a penta- instead of the hexammoniochloride should make any difference in the composition of the product in question. Moreover the appearance of tricobaltic tetroxide or of tetracobaltic pentoxide is quite unintelligible in the circum-

[*] Pelouze et Frémy, vol. iii. 1. p. 566.
[†] Silliman's American Journal, vol. xxiii. p. 256.

stances indicated, on any existing hypothesis. I should add that the black precipitate was found to contain traces of nitrogen and chlorine, but in far too minute proportion to estimate quantitatively.

The colourless liquid always contains free ammonia, sal-ammoniac, and cobalt (perhaps often wholly as chloride).

(1) 0·3086 grm. hexammoniochloride and 10 cubic centims. of water were heated in a sealed tube at 100° for forty-two hours. The filtrate, on treatment with standard hydric sulphate, furnished 0·05525 grm. free ammonia.

0·3086 grm. substance, similarly heated, gave a filtrate from which hot hydric and argentic nitrate threw down 0·4956 grm. argentic chloride.

(2) 0·29843 grm. yielded, in the manner already mentioned, 0·0527 grm. free ammonia.

0·29843 grm., treated as before, gave, on evaporation of the filtrate with hydric and platinic chloride, &c., 0·6265 grm. platinum.

These numbers indicate an almost complete decomposition, with a slight loss of ammonia :—

	Found.		Theory*.	
	I.	II.		
Free ammonia . .	17·90	17·66	18·99	per cent.
Total ammonia .	....	36·10	37·99	
Chlorine . . .	39·73	....	39·66	

In the following experiment the decomposition took place in presence of a somewhat greater relative quantity of water.

(X) 1·5204 grm. substance and 52·4 cubic centims. water were heated together at 90°–100° for forty-four hours in a soda-water bottle, the mouth of which was closed by a plug of caoutchouc kept tightly in its place by a screw and fittings. The slightly coloured filtrate was diluted with water to 500 cubic centims. Of these, 50 cubic centims. gave 0·01819 grm. free ammonia, 100 cubic centims. gave 0·4852 grm. argentic chloride, and 300 cubic centims., boiled with 2 grms. pure sodic hydrate, yielded a precipitate which was converted into 0·2156 grm. cobaltic sulphate. Hence the following percentages :—

Free ammonia . . 11·96
Chlorine . . . . 39·47
Cobalt in the filtrate 9·07

The invariable non-liberation of the whole of the ammonia,

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* Supposing the chlorine converted into sal-ammoniac and half the ammonia set free.

taken in connexion with the fact that a lower cobaltic oxide than the sesquioxide had been formed, naturally led me to look for hydric nitrate in the filtrates. The sodic solution just mentioned was evaporated to dryness, and hydric nitrate determined in it by Stein's method[*]. The percentage number obtained (0·06) is of sufficient value to show that the quantity of nitrate is extremely small, and adequate to account for only a minute fraction of the missing substance.

The presence of hydric nitrate in these liquids may also be shown qualitatively by boiling them with pure sodic hydrate until all free ammonia has been expelled, employing Harcourt's process, and applying Nessler's test to the distillate.

II. *Cobaltic β-Pentammoniotrichloride.*

The "purpureochloride" of Gibbs and Genth, which is still termed the "roseochloride" by French writers, may be conveniently designated by the above name, in accordance with its dynamical history. It can be prepared, as is well known, by adding potassic permanganate in slight excess to an ammoniacal solution of cobaltic chloride, and then boiling with abundance of strong aqueous hydric chloride. This process can be carried out on small quantities in a few minutes, and is already recognized as an excellent qualitative test for cobalt. It is, however, quite unsuited for quantitative work[†], as may be seen when the method is employed on a large scale; the filtrate contains cobaltic chloride and cobaltic hexammoniotrichloride in appreciable proportions and to a varying amount. Indeed no plan has yet been proposed whereby cobaltic chloride can be *at once* and *entirely* transformed into either of its polyammoniacal derivatives. Calcic oxychloride is an economical and convenient substitute for potassic permanganate in the preparation of the β compound. 5 parts of crystallized cobaltic chloride and 5 parts of sal-ammoniac are dissolved in 100 of water; the solution is cooled, mixed with 22 parts of strong aqueous ammonia and 2 parts of "chloride of lime," and allowed to stand freely exposed to air for twenty hours. At the end of that time the liquid is boiled with a large excess of strong aqueous hydric chloride and allowed to crystallize. The precipitate is the compound required. The very acid mother-liquid is poured off and employed as a precipitant in the next operation; after repeated use, it will contain a small quantity of the hexammoniotrichloride and a more considerable proportion of cobaltic chloride.

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[*] *Jahresbericht für Chemie*, 1851, p. 627.

[†] The contrary is maintained by Terreil, *Comptes Rendus*, vol. lxii. p. 139. Braun (*Zeit. analyt. Chem.* vol. v. p. 114) supports the view here adopted, but on other grounds.

Action of Water on Cobaltic β-Pentammoniotrichloride.—I have examined this reaction as it occurs in sealed tubes when heat is applied continuously for a long time.   The experiments and their results were, qualitatively, exactly the same as in the case already discussed; and I have to report that the analogous equation

$$2[5NH^3 . CoCl^3] + (3+n)H^2O = Co^2O^3 . nH^2O$$
$$+ 6(NH^3 . HCl) + 4NH^3$$
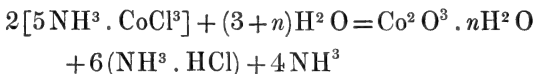
proved as untrue to fact as its predecessor.

0·7566 grm. of the brown-black precipitate, dried over oil of vitriol for six weeks, yielded, on treatment as described in the previous section, 0·0865 grm. water, 0·0940 grm. silica, and 1·1273 grm. cobaltic sulphate.

		Found.			Co^4O^5.
Cobalt . .	57·31	}	75·25	75·00
Oxygen .	18·84	}	24·75	25·00
Silica . .	12·42			
Water . .	11·43			
	100·00		100·00	100·00

The cobaltic oxide here formed is obviously identical in composition with that which is produced, under similar circumstances, from the hexammoniochloride.   The action itself, however, is generally slower and less complete than before, in consequence of the slight solubility of cobaltic pentammoniotrichloride in a weak ammoniacal solution of sal-ammoniac, wherein the hexammoniochloride dissolves with facility.   On this account, the *filtrate* from the brown-black oxide does not readily yield up all its chlorine on ebullition with hydric and argentic nitrate; and the total ammonia could not be estimated by the usual process with platinic chloride.   I will give two chlorine determinations which will prove the former point, and some determinations of the ammonia which is set free.

(1) 0·9952 grm. purpureochloride was heated with 50 cubic centims. water in a sealed tube for forty-eight hours at 80°–100°; 200 cubic centims. of the filtrate (1000 cubic centims.) gave 0·3285 grm. argentic chloride.

(2) 0·3000 grm. substance and 10 cubic centims. water, at 90°–130° for forty-three hours, gave 0·4618 grm. argentic chloride.

(3) 100 cubic centims. of the filtrate in (1) contained 0·01003 grm. free ammonia.

(4) 0·4015 grm. substance and 10 cubic centims. of water, at 100° for forty-two hours, furnished 0·0459 grm. free ammonia.

(5) Experiment (2) was repeated, the time being forty-five hours. The free ammonia amounted to 0·02482 grm.

(6) 0·4015 grm. chloride and 10 cubic centims. water, at 90°– 130° for forty-seven hours, gave 0·03485 grm. free ammonia.

Found.

	(1)	(2)	(3)	(4)	(5)	(6)	Theory*.
Chlorine	40·83	38·08	....	....	....	....	42·35
Free ammonia.	....	....	10·08	11·43	8·27	8·68	13·52

If we make the useful assumption that none of the chlorine in (1) was obtained from undecomposed substance in the filtrate, it appears from the operation

$$\left(0{\cdot}1003 \div \frac{0{\cdot}9952 \times 40{\cdot}83}{42{\cdot}35}\right) \times 100$$

that 10·45 is the real percentage in (3). This assumption is probably sufficiently in accordance with fact to allow us to believe that the whole of the ammonia which should become free does not make its appearance; and the conclusion follows *à fortiori* from a similar comparison of experiments (2) and (5) :

$$\left(0{\cdot}2482 \div \frac{0{\cdot}3000 \times 38{\cdot}08}{42{\cdot}35}\right)100 = 9{\cdot}2 \text{ per cent.}$$

Hydric nitrate, cobaltic chloride, and sal-ammoniac were proved to exist in the "filtrate;" and the entire decomposition is evidently in perfect accordance with that described in the preceding section.

III. *Cobaltic α-Pentammoniotrichloride.*

This compound, the "roseochloride" of Gibbs and Genth[†], is the first of these ammoniotrichlorides in order of formation. According to the account given by its discoverers, it is not easy to obtain in the pure state—that is, free from the β-chloride just referred to. I have procured it without any difficulty in the following way :—5 grms. of crystallized cobaltic chloride are dissolved in water with the aid of heat; the solution is cooled, diluted to 90 cubic centims., and mixed in rapid succession with 27·5 cubic centims. strong aqueous ammonia, and 2·5 grms. potassic permanganate dissolved in 100 cubic centims. water. The temperature of the liquids before mixing should not exceed 18°. After standing for twenty-four hours in a wide beaker, with free exposure to air, the solution is filtered from its manganic deposit, neutralized with ordinary aqueous hydric chloride

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* Supposing the whole of the chlorine converted into sal-ammoniac and the excess of ammonia liberated, as in the equation last given.

† Silliman's American Journal, vol. xxiii. p. 241.

to which two volumes of water had been added, and finally pre-
cipitated with a cold mixture of three volumes of aqueous hydric
chloride and one-third of a volume of spirit. After washing
with a fresh quantity of the precipitating mixture, then with
alcohol, and drying in the air, the compound corresponds very
closely in composition with its formula, as may be seen from the
annexed determinations.

0·3598 grm. substance lost 0·0237 grm. at 100°, and gave
0·2085 grm. cobaltic sulphate.

	Found.	$5NH^3 . CoCl^3 . H^2 O.$
Water . .	6·59	6·68 ⎫
Cobalt . .	22·29	22·26 ⎬ per cent.

On boiling a solution of the chloride with a trace of hydric
chloride, it immediately underwent its remarkable transformation
into the purple isomer. Neither potassic iodide nor potassic
chromate produced any precipitate with it; potassic dichromate
yielded a brick-red precipitate. These are the reactions of the
pure chloride.

["*Crystallized Cobaltic Chloride.*"—I have not been able to find
any reliable statement of the composition of hydrous cobaltic chlo-
ride crystallized from water. It is so much more convenient, for
many preparations, to weigh cobalt in this form, that I have
determined the cobalt and water in the crystals. The substance
was prepared for analysis by igniting the β-ammoniotrichloride,
dissolving the black residue in aqueous hydric chloride contain-
ing a little hydric nitrate, repeatedly evaporating first with hy-
dric chloride and then with water, and ultimate crystallization
from the last-named solvent. After thorough drying by the aid
of pulverization and pressure between folds of bibulous paper,
the following numbers were obtained :—

0·3410 grm. substance lost (1) 0·1030 grm. over oil of vitriol,
and subsequently (2) 0·0510 grm. at 100°. The residue, evapo-
rated with hydric sulphate and ignited, furnished 0·2246 grm.
cobaltic sulphate.

	Found.	$CoCl^2 + 6H^2 O.$	
Cobalt . . .	25·33	25·10	
Chlorine . . .	. . . .	29·71	
Loss (1) . . .	30·20	30·13	$4H^2 O$
Loss (2) . . .	14·96	15·06	$2H^2 O$
		100·00	

Commercial "pure chloride of cobalt" has very nearly the same
composition.]

IV. *Theoretical Considerations.*

(1) The action of water upon the polyammoniacal cobaltic chlorides would be intelligible without further delay, if it consisted merely in the production of sal-ammoniac, hydrous dicobaltic teroxide, and ammonia. Equations in accordance with this hypothesis have been shown, however, not to correspond with experiment. Abundance of sal-ammoniac is, indeed, invariably formed; but tetracobaltic pentoxide is the oxide precipitated, and the ammonia which is not required to constitute sal-ammoniac is never wholly recoverable in the free state.

The constant afterpresence of a minute quantity of hydric nitrate and cobaltic chloride furnish, I believe, a key to this problem, which may be interpreted as follows. In the first place, the equation* of movement (which must not be understood statically),

$$2[CoCl^3 . 5NH^3] = 2CoCl^2 + 10NH^3 + Cl^2, \quad . \quad . \quad (a)$$
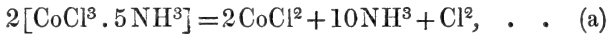
expresses the momentary genesis of cobaltic chloride, ammonia, and chlorine as such. The two latter act upon each other so as to form (nitrogen?) ammonia, hydric nitrate, and sal-ammoniac, whereby they arrive at a permanent condition of repose. The cobaltic chloride attains that condition only after performing work which may be formulated thus:—

$$\left. \begin{aligned} 2CoCl^2 + 2[CoCl^3 . 5NH^3] + (5+n)H^2O = Co^4 O^5 . nH^2O \\ + 10[NH^3 . HCl]. \dots \dots \dots \end{aligned} \right\} \quad (b)$$
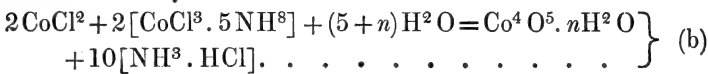
A fresh portion of the original substance hereupon assumes the properties of transference indicated in (a), and then the statical properties pointed out in (b) and the text immediately preceding it. But as (a) is necessarily in advance of (b), it is evident that a small amount of cobaltic chloride must eventually remain at the close of the reaction. The proportion of chlorine available for oxidizing-purposes is one-sixth of all that is present, and is equivalent to 1·02 per cent. of ammonia for the hexammoniochloride, on the hypothesis

$$3Cl^2 + 2NH^3 = N^2 + 6HCl,$$

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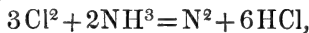
* This is the simplest equation suitable for the purpose. But as I find that cobaltic sesquioxide and sal-ammoniac, when digested under pressure with water, give rise to traces of cobaltic chloride, those who prefer it may adopt the systems

$$2[CoCl^3 . 5NH^3] + (3+n)H^2O = Co^2 O^3 . nH^2O + 6[NH^3 . HCl] + 4NH^3$$

and

$$Co^2O^3 . nH^2O + 6[NH^3 . HCl] + 4NH^3 = 2CoCl^2 + 10NH^3 + (3+n)H^2O + Cl^2$$

instead of (a). They amount nearly to the same thing, and are possibly better than the single equation given above.
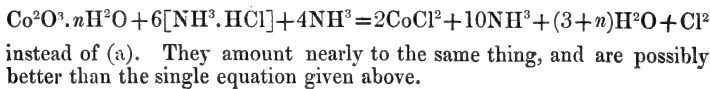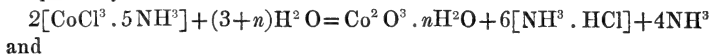
or to 0·38 per cent. for the equation

$$4\,Cl^2 + NH^3 + 3\,H^2O = HNO^3 + 8\,HCl.$$
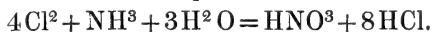
It has been seen, however (continuation of Exp. X, Sect. I.), that the actual yield of hydric nitrate is not by any means accordant with the number (1·41) which flows from the latter consideration; neither does the corresponding quantity of ammonia neutralized and oxidized in nitrification ($HNO^3 : 9\,NH^3 :: 0\cdot06 : 0\cdot14$) go far to account for the loss. The same experiment fortunately suggests an additional explanation. On comparing the percentage of free ammonia found with that indicated by theory, there is a difference of $18\cdot99 - 11\cdot96 = 7\cdot03$, which number is to the cobalt in the filtrate (9·07) nearly as $6\,NH^3$ to Co^2. It may be inferred that the compound

$$[2\,CoCl^2 + 2\,(CoCl^3 \cdot 6\,NH^3)]$$
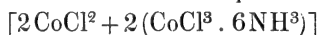
really existed in the filtrate, and that through its agency tetracobaltic oxide was formed,

$$\left.\begin{array}{l}[2\,CoCl^2 + 2\,(CoCl^3 \cdot 6\,NH^3)] + (5+n)\,H^2O = Co^4O^5 \cdot n\,H^2O \\ +\, 10\,(NH^3 \cdot HCl) + 2\,NH^3. \quad \ldots \ldots\end{array}\right\} \quad (c)$$
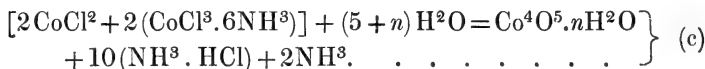
It is not improbable that this equation holds good also for the pentammoniochloride to a certain extent, especially when we remember that the hexammoniochloride is necessarily produced by the ammonia which remains free throughout the reaction, when the former chloride is decomposed by hot water: and I need not point out that equation (b) receives, on this ground, great additional strength. A special experiment showed that the following mixture, viz.

> 0·13425 grm. hexammoniochloride . . $2\,(CoCl^3 \cdot 6\,NH^3)$,
> 0·06550 grm. anhydrous cobaltic chloride $(2\,CoCl^2)$,
> 20 cubic centims. water,

is comparatively stable, and is far from undergoing complete decomposition when heated under pressure for forty-seven hours to 80°–100°; the presence of the supposed compound in any one of the filtrates is therefore what might be expected under the circumstances which have been described. It may, then, be said that the oxidation of ammonia to hydric nitrate, and the combination or mutual presence of cobaltic chloride and hexammoniotrichloride are sufficient causes to account for the nonappearance of the expected ammonia: any deficiency not arising from these sources must be attributed to incomplete decomposition.

(2) The above considerations induced me to investigate the action of cobaltic chloride on the β-pentammoniochloride and hexammoniochloride.

β-Pentammoniochloride.—The conditions that the filtrate shall be neutral are

$$2 \, CoCl^2 + 2 \, (CoCl^3 . 5 \, NH^3) + (5 + n) \, H^2 O \, ;$$
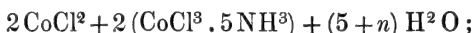
which give these results,

$$Co^4 O^5 . n H^2 O + 10 \, (NH^3 . HCl).$$
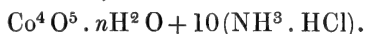
1·4847 grm. pentammoniochloride and 0·77454 grm. cobaltic chloride* were boiled in an open beaker with 318·25 cubic centims. water for three quarters of an hour.   The precipitate, dried at 70°–80°, weighed 0·8199 grm.; 0·2705 grm. of it gave 0·01825 grm. water and 0·46675 grm. cobaltic sulphate. Hence the composition of the precipitate was

	Found.		$Co^2 O^3$†.	$3Co^2 O^3 . 2H^2 O.$
Cobalt . .	66·37 ⎱	⎰ 71·17	71·43	66·67
Oxygen . .	26·88 ⎰	⎱ 28·83	28·57	26·66
Water . .	6·75	. . . .	. . . .	6·67
	100·00	100·00	100·00	100·00

Also the amount of cobalt   grm.

due from the ammonio-chloride is . 0·3542

    ,,   ,,   chloride is . . . . 0·3547

Total . . . . . 0·7089

found in the precipitate was . . . 0·5442

The evolution of a small quantity of ammonia during ebullition was the only very noticeable feature in the reaction.   Its occurrence is evidently owing to the interference of the products of decomposition with each other.   The precipitation of dicobaltic teroxide instead of tetracobaltic pentoxide was manifestly due to atmospheric oxidation; and the numbers show that considerably more than half of the cobaltic chloride was decomposed.   The discrepancy between the statement of Frémy and that of Gibbs and Genth (see Sect. I.) probably finds its solution here,—it being quite possible that the former chemist applied heat for a considerable time to the liquid with which he worked, and thereby obtained the sesquioxide; while the latter, having dealt with a gentler reaction, may with equal likelihood have obtained the magnetic oxide.

I have repeated the above experiment in a closed vessel.

0·8094 grm. pentammoniochloride, 0·4225 grm. cobaltic chloride‡, and 64·5 cubic centims. water were heated together

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* The excess is intentional: 0·77334 grm. is the theoretically equal amount.

† $2Co^2O^3 = Co^4O^5 . O.$

‡ 0·4216 grm. is the calculated quantity.

for forty-eight hours at $100°$. The precipitate, dried as before, weighed approximately $0·5770$ grm.; $0·2663$ grm. of it gave $0·0137$ grm. water, $0·0150$ grm. silica, $0·4467$ grm. cobaltic sulphate. The composition of the precipitate was—

	Found.		$3Co^2O^3.CoO.$
Cobalt . .	$64·52$⎱ ⎰$72·31$		$72·41$
Oxygen . .	$24·71$⎰ ⎱$27·69$		$27·59$
Silica . . .	$5·63$		
Water . . .	$5·14$		
	$100·00$	$100·00$	$100·00$

The amount of cobalt due from the ammoniochloride is $0·1931$ grm.

   ,,   ,, chloride is . . $0·1935$

            Total . . . $0·3866$

  ,,   found in the weighed precipitate was $0·3723$

The filtrate contained $0·0082$ grm. free ammonia; it gave no precipitate with ammonic polysulphide,—a result which is quantitatively corroborated by the above numbers. As in the former case, there has been considerable oxidizing action from external sources, viz. the air in the closed vessel and the hot air in the desiccating bath; yet this has not proceeded to such an extent as to mask entirely the real nature of the process. Although the oxide Co^4O^5, as *thus* generated, is evidently more prone to oxidation than as at first obtained, yet the oxide actually analyzed still shares with it the property of deriving at the same time from cobaltic dichloride and terchloride.

Hexammoniochloride.—The conditions and results of neutrality are

$$3CoCl^2 + 2(CoCl^3 . 6NH^3) + (6+n)H^2O = Co^5O^6 . nH^2O$$
$$+ 12(NH^3 . HCl). \quad . . . . \Big\}(d)$$
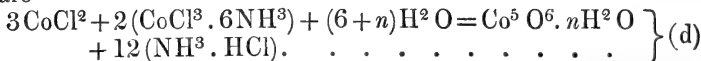
$0·40275$ grm. hexammoniochloride, $0·29475$ grm. cobaltic chloride, and 75 cubic centims. of water were digested for fifty hours at $90°$, in sealed tubes, without undergoing much alteration; but on further heating for forty-seven hours at $110°–120°$, complete decomposition ensued. The precipitate, dried at $100°$, weighed approximately $0·3602$ grm.; $0·3335$ grm. of it gave $0·0161$ grm. water, $0·0463$ grm. silica, and $0·5139$ grm. cobaltic sulphate. The composition of the precipitate was—

	Found.		$2Co^2O^3.CoO = Co^5O^6.O.$
Cobalt . .	$59·27$⎱ ⎰$72·91$		$72·82$
Oxygen . .	$22·02$⎰ ⎱$27·09$		$27·18$
Silica . . .	$13·88$		
Water . .	$4·83$		
	$100·00$	$100·00$	$100·00$

grm.

Also the amount of cobalt in the ammoniochloride taken was 0·0900

„ „ chloride „ 0·1350

Total . . . . 0·2250

„ found in the weighed precipitate was 0·2135

The filtrate, which was colourless, yielded a brown coloration with ammonic polysulphide, and contained 0·00846 grm. free ammonia. The susceptibility of these mixed oxides to oxidation, when prepared by the direct intervention of cobaltic chloride, is again evinced in the composition of this precipitate, which, however, contains the desired oxide in no higher state of oxidation than that of the next degree (see equation at the foot of p. 257).

The following experiment is important.

0·13425 grm. hexammoniochloride, 0·0655 grm. cobaltic chloride, and 20 cubic centims. water were placed together in each of three sealed tubes, and heated to 80°–100° for forty-seven hours. [The cobaltic reagents are in the ratio $2(CoCl^3 . 6NH^3) : 2CoCl^2$.] Such part of the precipitate as could be collected weighed 0·19 grm. when dried at 65°; 0·1715 grm. of it gave 0·0092 grm. water, 0·0259 grm. silica, and 0·2552 grm. cobaltic sulphate— numbers which show that it had been almost wholly converted into dicobaltic teroxide.

	Found.		$Co^2 O^3$.
Cobalt . .	57·23	71·95	71·43
Oxygen . .	22·31	28·05	28·57
Silica . .	15·10		
Water . .	5·36		
	100·00	100·00	100·00

The filtrates were *neutral,* and contained the original substances together with sal-ammoniac. The filtrates from two of the tubes were united, evaporated to dryness with a little hydric chloride, and the cobaltic chloride extracted from the residue by alcohol, and converted into 0·0382 grm. sulphate; the residual hexammoniochloride was transferred to a weighed filter and dried at 100°; it weighed 0·1369 grm. An easy calculation, based on these results, shows that the ammoniochloride and chloride *engaged in the reaction* were to each other in the ratio 2 : 3·08, which is in sufficient accordance with the ratio 2 : 3 already laid down in equation (d) as the condition of obtaining a neutral filtrate.

(3) When either of the polyammoniacal chlorides referred to in this memoir is decomposed by water at 60°–120° under pressure, the glass vessel employed is powerfully attacked. When

ordinary soft glass which contains lead is used, the brown-black precipitate separates, for the most part, in beautiful lustrous scales, and contains from 13 to 15 per cent. of silica; if hard glass be substituted, the precipitate is destitute both of lustre and of scaly appearance, and does not contain more than about 5 per cent. of that substance. Special comparative experiments were made with aqueous ammonia of such a strength as the filtrates from these precipitates were found to possess; but it was found that there was no action on soft glass, and no diminution in the ammoniacal standard. Some of the precipitates were digested in sealed tubes with aqueous ammonia under like conditions; but the glass was not at all corroded. Dicobaltic teroxide and very strong aqueous sal-ammoniac, however, did attack the tube slightly, and a little cobaltic chloride was formed, at the same time. It is the extent, not the nature, of such an action which is surprising. The hydrates

$$\beta \, CoCl^{3-n}(HO)^n \, . \, 5 \, NH^3,$$
$$CoCl^{3-n}(HO)^n \, . \, 6 \, NH^3,$$
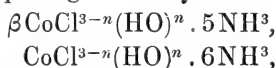
however ephemeral their existence under the circumstances, ought to be much more energetic in their action upon glass than potassic hydrate.

(4) In section I. it is stated that the precipitates which have just been alluded to, as well as dicobaltic teroxide (the product of their complete oxidation), can be, to a great extent, transformed into hexammoniochloride by digestion with sal-ammoniac and aqueous ammonia. In the case of dicobaltic teroxide, we have the process of preparation of this valuable compound in its most general form, the other methods given being manifestly equivalent to this in their essential details. Either this process, or the substitution in it of a chloride and a powerful oxidizing agent for a peroxide, may prove to be useful in the future as a means of obtaining polyammoniacal derivatives, if required. I may mention, however, that I have not met with satisfactory results on applying this method to nickel sulphate or zinc chloride, or by heating aqueous aniline or pyridine with sal-ammoniac and dicobaltic teroxide.

(5) When aqueous aniline, pyridine, or ethylamine (though in this last case the experimental data have not been as numerous as I could desire) is digested with cobaltic β-pentammoniochloride under pressure, no analogue of the hexammoniochloride is formed, but the hexammoniochloride itself, together with the usual products of the decomposition of the pentammoniochloride by heated water. As in these experiments no ammonia was employed, it follows that the ammonia which gave rise to the hexammoniochloride must have proceeded from the pentam-

moniochloride; and that, consequently, that ammonia which constitutes the difference between them is not the same in properties as free ammonia. Hence, as has been already seen, ammonia does not convert the pentammoniochloride into hexammoniochloride unless water be present to effect a decomposition.

(6) If we consider the nature of the oxides which these polyammoniacal cobaltic chlorides generate when decomposed by heated water, we shall perceive that the formulæ of the latter ought to be doubled,—the argument being in principle the same as that for doubling the formula of ferric chloride if it were written $FeCl^3$. The illegitimacy of rational formulæ having the general character

$$x\mathrm{NH}^3 . \mathrm{CoCl}^3$$
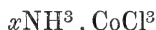
for these bodies is also evident when we call to mind that an ammoniacal salt and an oxidizing agent are not only their producers, but their products of decomposition,—facts to which such formulæ do not refer, while they represent reactions which have not yet been recorded by a single experimenter.

XXIX. *Synthesis of White Light from the Colours of the Spectrum.* By C. J. WOODWARD, *B.Sc.*

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

THE following demonstration of the synthesis of white light is, I believe, new; it occurred to me one evening when using Newton's disk.

The spectrum from a bisulphide-of-carbon prism was thrown, by means of a small mirror held in the hand, on to a screen; on moving the mirror to and fro so as to cause the spectrum to move over itself in the direction of its length, there was formed a band of white light, identical in appearance with a beam of white light received direct from the source of light and then similarly thrown upon the screen by the moving mirror.

By using suitable diaphragms, so as to stop out certain colours, the compound colour resulting from the remaining colours may of course be shown.

<div style="text-align:right">

I am, Gentlemen,
Your obedient Servant,
C. J. WOODWARD.

</div>

Midland Institute, Birmingham,
   March 11, 1868.

XXX. *Investigation of the Alteration produced by Heat in the Velocity of Propagation of Light in Water.* *By* RICHARD RÜHLMANN[*].

[With a Plate.]

I. *Critical Review of previous experimental Researches.*

THE fact has been long known that the refraction of light, especially in liquids, is affected by heat. The first numerical results in proof of this which attained publicity, were probably those got by Baden Powell[†] in determining the refractive index of oil of cassia at different temperatures; although Arago[‡], by means of his interference-refractor, had already instituted an examination on the change in the refractive index of water between 0° and 10°. Arago's results are ambiguous. Making use of the same apparatus, with only slight modifications, Jamin[§] afterwards undertook an investigation of the index of refraction of water, and found a well-marked decrease in the refractive index with the temperature[||]. He further observed that the refraction has not, like the density, a maximum at 4° C., but continually diminishes from 0° upwards, a diminution which may be represented by

$$K_t = K_0 - at - bt^2,$$

where K_t denotes the index of refraction at $t°$, K_0 the same at 0°, and a and b are constants.

Chronologically after this appeared the investigation of Van der Willigen[¶], who, by means of Meyerstein's spectrometer, measured a series of the refractive indices of distilled water at different temperatures. These measurements are, however, so few in number, and are confined within such a narrow thermal range, that we need here do no more than mention them.

Induced by the experiments of Baden Powell, who was fully alive to the importance of knowing the variations of the refractive index with the temperature, Gladstone and Dale undertook a rather elaborate investigation of this subject, and published

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[*] Translated from Poggendorff's *Annalen*, vol. cxxxii. pp. 1 & 177, by Frederick Guthrie, F.R.S.E., Professor of Physics and Chemistry, Royal College, Mauritius.

[†] Poggendorff's *Annalen*, vol. lxix.

[‡] Arago's *Sämmtliche Werke, deutsch, von* Hankel, vol. x. pp. 257 &c., and p. 247. He finds that warm water refracts light more powerfully than cold water.

[§] " Description d'un nouvel appareil de recherche fondé sur les interférences," *Comptes Rendus*, vol. xlii. pp. 482–485.

[||] Jamin, " Sur la vitesse de la lumière dans l'eau à diverses températures," *Comptes Rendus*, vol. xliii. pp. 1191–1194.

[¶] Poggendorff's *Annalen*, vol. cxxii. pp. 190–192.

their results " On the Influence of Temperature on the Refraction of Light " in the Philosophical Transactions*. These investigators made use, for their purpose, of the apparatus of Baden Powell†, and made determinations (for water between 0° and 80°·6 C., for bisulphide of carbon between 0° and 42°·5 C., and for various alcohols and ethers between 0° and 70° C.) of the alteration of the refractive index for Fraunhofer's lines A, D, H. The results arrived at are collected in the following propositions.

(1) All substances, by increase of temperature, show a diminution in the refractive index. The magnitude of the alteration varies with various substances, being least in the case of water, greatest in that of bisulphide of carbon.

(2) The length of the spectrum diminishes rapidly with the temperature in the case of substances which refract light powerfully, such as bisulphide of carbon, phosphorus, &c.; this diminution is scarcely perceptible in the case of water.

(3) In the neighbourhood of the point of change of the state of aggregation no remarkable change occurs in the nature of the alteration of the index.

The above conclusions have reference to the relation between density and refractive index; we shall return to this point again at the end of the present paper. The extent of the investigations of these two physicists is certainly very great, and great abundance of material is presented. But the validity of their results is open to doubt, because it is absolutely essential that the measurements should be exact to one unit in the fourth decimal place, and this exactness is not attained. For water, two determinations of the D line at 0° C. are given,

0° C. . . . . 1·3330 and 1·33374 (Rühlmann 1·33374).

While the first of these numbers forms the starting-point for a series of determinations from 0° to 70° C., advancing continually by 5° C., the second is obtained from a small number of observations (which are said to be *most careful*) in order to verify Jamin's result, that the index of refraction does not show any singularity at 4° C. corresponding with the maximum density. My own observations, after elimination of accidental errors, gave at 0° C. a result perfectly agreeing with Gladstone's more correct number. It hence follows that the first number is too small by 7 units of the fourth decimal place.

For 70° C. for the D line, these two physicists gave

70° C. . . . 1·3237 (Gl. and D.), (1·32505 R.),

a value again too small, according to my experiment. The results moreover differ very widely from Baden Powell's and

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* Philosophical Transactions for 1858, pp. 887–894.
† Described and figured in the Report of the British Association for 1839.

Fraunhofer's results—much more so than mine. This fact, taken in conjunction with the great discrepancy between different observations made under like circumstances, throws an unfavourable light upon their accuracy. On this account it was not possible for me to regard the problem as solved—the less so because Gladstone and Dale had not even taken the trouble to deduce a law in the form of an interpolation formula from their experiments. It is not possible to determine the source of the above pointed out inexactness, because the numbers upon which the results are based are nowhere given, and we are thus debarred from the detection of any possible considerable error arising from inadvertence or miscalculation.

The next investigation which must, at all events for the sake of completeness, be mentioned is by Schmidt[*], who had occasion to determine the line D for water and certain saline solutions. In the first place, the graduation was insufficient on the circle by which the angular measurements in these experiments were made. In the second place, the hollow prism containing the liquids was taken to pieces from time to time, its angle, however, being determined only at starting, and there being no guarantee of its remaining constant during the observations. The numbers obtained in this manner certainly deviate enormously from all others; for instance, for D,

For 0°·9 C. . . . . 1·3355 (Sch.) instead of 1·3337 (R.).

Although Dr. Schmidt was obliged himself to admit the untrustworthiness of his results, he still decided to explain the want of accord by the assumption that the sodium-line which he used for D did not coincide with D, but lay so between D and E that its distance from D was to its distance from E as 135 to 92. If we consider how thoroughly well established, not only by Fraunhofer but by Kirchhoff, is the coincidence of the sodium-line with the characteristic double line D, we may conversely conclude how little weight is to be attached to Schmidt's determination of the refractive indices.

Much greater importance is to be attached to the observations of Landolt on the alteration of the refractive power with the temperature, which are contained in his valuable experimental research " On the Influence on the Velocity of the Propagation of Light exercised by the Composition of Liquid Compounds containing Carbon, Hydrogen, and Oxygen "[†]. His observations relate chiefly to their different temperatures and the three

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[*] Pogg. *Ann.* vol. cvii. pp. 204 &c. "Auszug aus dem Programm des Gymnasiums und der damit verbundenen Realschule zu Plauen für das Jahr 1859."

[†] Pogg. *Ann.* vol. cxxiii. p. 595.

most brilliant lines (α, β, γ according to Plücker) of the spectrum of incandescent hydrogen gas. Landolt's results, in the main, confirm those of Gladstone and Dale, but are not sufficient for our purpose, because they are not extended over a sufficient range of temperature.

Fizeau[*], by employing the method of interference, measured the alteration in the rate of propagation in glass, fluor-spar, Iceland-spar, and afterwards in rock-crystal; and his experiments are of the greatest importance and admirable in regard to their execution. Fizeau, however, in his method confined himself to observations of the homogeneous light of the sodium-flame; so that from them no conclusion can be drawn concerning an alteration in the dispersion. Since these experiments are of great importance, and furnish the only hitherto given numerical data for the alteration of the velocity of propagation in solid bodies, I may be allowed to describe them briefly here. If we denote the index of refraction for the ordinary temperature by n, that for increased temperature by n'; further, if v denote the velocity of light in air, v' its velocity in the cold, and v'' in the warmed body, and if we put

$$v'' = v'(1 + \beta t),$$

then

$$\beta = \frac{n - n'}{n}.$$

The following are the results:—

Substance.	Density.	n_{D}.	$(n' - n)_{100}$.	100β.
Glass from St. Gobains ...	2·438	1·5033	0·000163	−0·000108
Glass from St. Gobains, second sort .... }	2·514	1·528	0·0000997	−0·000065
Crown glass	2·626	1·5204	varies irregularly.	
Fluor-spar	3·2	1·435	−0·00136	+0·00049
Flint glass (common) ...	3·584	1·6112	0·00026	−0·00163
Flint glass (heavy)	4·14	1·682	0·000687	−0·000408
Iceland-spar (cut parallel to the axis) ...... }	2·723	o 1·65850 e 1·46835	+0·0000565 +0·00108	−0·0000341 −0·000727

Fizeau's experiments therefore give, with the exception of fluor-spar, the following result, that, in spite of the diminution of density, *the velocity of the propagation of light diminishes, and therefore the refractive power increases as the temperature increases.*

In fluor-spar alone the index of refraction diminishes with increase of temperature, as is the case with liquids and gases.

An explanation and solution of this peculiar contradiction is subsequently attempted.

The method adopted by Fizeau to determine the numbers he obtained is the following :—

The substance is cut into plates whose parallel surfaces are about 1 to 10 millims. apart. A pencil of homogeneous light falling perpendicularly upon the plate gives rise to two reflected rays (repeated reflexion being neglected) which produce phenomena of interference. Since most surfaces which the mechanical optician endeavours to grind flat are almost invariably more or less convex, the interference-fringes have usually a circular form. The difference of path of the two luminous rays is caused by the fact that the first is reflected directly at the front surface of the glass, while the second, entering the glass and being reflected at the back surface of the plate, has to pass backwards again through the thickness of the glass to reenter the air. We have accordingly here to consider the difference of the velocity with which the paths in the air and in the glass are traversed, and the difference of phase suffered through the reflexion. When the plate is warmed, the fringes are of course moved ; and this motion is measured. This motion is owing to two causes : (1) an expansion of the plate perpendicular to its surfaces, and a consequent alteration in its thickness and consequently of the path ; (2) an alteration in the index of refraction itself, whereby the velocity is altered with which the ray traverses the altered path. If the thickness of the plate at a given temperature is known, we can deduce the alteration in the index from the number of the displaced fringes.

The chief difficulty in applying this otherwise so excellent method lies in the impossibility of determining the coefficient of expansion with perfect accuracy. For the exact description of the experimental arrangement and of the formulæ by help of which the results are derived from the experiments, we must refer to the interesting original paper.

A further investigation in this field is furnished by a second research of the two English physicists, Gladstone and Dale[*], which consists partly of fresh determinations of the indices of refraction at different temperatures, but is chiefly concerned in discussing the relation between index of refraction and density, the difference of refractive power in liquids of homologous series, and the effect of the introduction of new radicals. This investigation offers an extraordinary amount of new observations,

[*] "Researches on the Refraction, Dispersion, and Sensitiveness of Liquids," Philosophical Transactions, 1863, vol. clviii. pp. 318-343.

namely the refraction indices for seventy-six substances for the
Fraunhofer's lines A, D, H, mostly for three temperatures be-
tween 5° and 36° C., and, further, the indices for sixty-eight
liquids for intermediate temperatures, and for all the principal
lines of the spectrum. This investigation has, moreover, a greater
value than the preceding one, because it furnishes us with a
ready means of judging of the correctness of the experiments.
The determinations were made in a hollow glass prism, and the
refractive angle was assumed to be constant at about 61° at the
different temperatures; whereas in their previous investiga-
tion Gladstone and Dale sought to determine the angle of least
deflection at temperatures previously fixed upon, as 0°, 5°, 10°,
20°, &c. : these measurements, in their new investigation, were
made at the temperatures which actually presented themselves
during the process of heating or cooling. The latter method
must certainly give results of far greater accuracy than the former
one. They estimate the error in their thermal data at 1° or
2° C., which, however, in water of high temperatures causes a
variation of $+8$ units in the fourth decimal place. They give
the exactness of their angular measurements at $\pm 1'$, which cor-
responds to an error of ± 2 units in the fourth decimal place.
We thus see that a variation of ± 8 units of the fourth decimal
place may be very easily accounted for. They give the name
"*sensitiveness*" to the alteration in the refractive index n with
the temperature within 10° C.; and $n-1$ is called the refractive
energy. The diversity in the numbers given for the refractive
index for water for the D line for 0° is not explained. In
order to compare the agreement or disagreement of Gladstone
and Dale's observations for water with mine, their results in re-
gard to the D line have been marked with little crosses in Plate V.,
in which the change of the index in regard to the temperature
is represented graphically. I shall return again in the sequel
to the view which these physicists take of the relation between
the density and the indices of refraction.

Finally, I have to mention a series of experiments by Müt-
trich* on the alterations caused by heat in the indices of refrac-
tion in rape-oil and water. To determine these values, Müttrich
employed the alteration in the optical axis of Arragonite in the
liquid after its alteration in the open air had been very exactly
measured. The determinations gave results far too high, although
the observations for the sodium-line agree very well with the

* " Bestimmung des Krystallsystems und der optischen Constanten des
weinsauren Kalinatrons, Einfluss der Temperatur auf die optischen Con-
stanten desselben und Bestimmung des Brechungsquotienten des Rüböles
und des distillirten Wassers bei verschiedenen Temperaturen, von A. Müt-
trich," Pogg. *Ann.* vol. cxxi. pp. 193–238, and pp. 298–430.

formula
$$n = 1\cdot33696 - 0\cdot00006909t - 0\cdot0000008513t^3.$$

As this method requires the exact determination of the law of alteration of the angle of the axis of the crystalline plate, and is therefore rather complicated, and, further, as every error in the determination of this law is introduced into the determination of the index, I do not think that the method will receive very extensive application to the determination of the dependence of the refraction of liquid bodies upon their temperature. These observations relating to Fraunhofer's line D and water are marked in Plate V. by crossed circles.

If we cast a glance back at the above experimental researches which have been hitherto published, we are forced to admit that the chief fundamental facts have been indeed established by Fizeau for solid bodies and by Gladstone and Dale for liquid ones, but that the results are, to a very considerable extent, deficient in accuracy. The question cannot be regarded as solved until not only the refractive index (with exactness within certain limits), but also the law of alteration has been given in the form of an interpolation formula. This interpolation formula is best given in the shape

$$\mu_t = a + bt + ct^2 + dt^3 + et^4 + \ldots,$$

where the constants a, b, c, d, &c. have been determined with the greatest accuracy and the agreement of the formula with the observations has been established. For solid bodies, Fizeau has furnished these data, while for liquids the only data hitherto given are those of Müttrich, and these merely between $0°$ and $65°$ C. The numbers of the latter observer differ so much from those of other physicists, that, in spite of their great extension, they can at most only be regarded as relatively true, inasmuch as they must all be affected by a common error, about which we do not even know whether it may not be a function of the temperature.

The problem which is here first to be solved is accordingly to give a formula, either for the alteration of the index of refraction for different luminous rays for as many liquids as possible, or preferably for the constants of a dispersion formula.

I have endeavoured to give these data for water; and after I have tested my method by this investigation, I shall seek to determine these important physical constants for other substances.

It appears, from what has been stated above, that it is of as little avail to determine the refraction-indices of substances without giving the formula of alteration as it is to give the specific gravity without adducing the coefficient of expansion.

II. *The Methods of Observation.*

For the determination of the index of refraction many methods may be adopted; for almost every optical relation, in which the velocity of the propagation of light is concerned, may be used as the base of such a method. The most common of these methods is that founded upon the measurement of the deviation which a ray of light experiences in passing through a prism of the substance under investigation. This process is employed in my experiments, and will be discussed subsequently.

The second method, only employed by Arago* and Jamin and lately also by Fizeau, is the method of interference. If we allow two rays of common or homogeneous light to come together under favourable circumstances in directions either parallel or inclined at a small angle to one another, it is well known that phenomena of interference occur which in general are parallel bands when the common source of both rays is a line. If we examine two rays of light which give rise to such phenomena, we find, as is well known, a central bright band at the place where both systems of waves have passed over exactly equal lengths from their departure from the common source of light. If, now, one of the rays is delayed, it is later in reaching the point where the central band was previously produced: this band can no longer be found in the middle, but will be displaced a little towards the side of the impeded ray. This fact enables us to determine the velocity of propagation of light in a medium if we know exactly the thickness of the impeding layer, and accurately measure the displacement of the middle band by a micrometer arrangement, or by angular measurement by means of a telescope.

By this means we can detect extremely minute differences in the refractive power; and the method is very useful for differential observations. But the apparatus can no longer be employed when the differences are great, unless we can effect a determinable hindrance in the second ray as well as in the first. For this purpose, in his apparatus Arago made use of a compensating arrangement, the action of which depended upon the second ray of light being made to pass at a measurable angle through a parallel-sided glass plate of known thickness, by which means it suffered an exactly determined retardation. We shall not describe Arago's apparatus more minutely, because it has scarcely been applied to quantitative experiments; and we need only indicate the principle of the modified interference-refractors which Jamin employed for his observations†. This instrument depends upon

* Arago's *Sämmtliche Werke, deutsch, von* Hankel, vol. x. p. 257, *ff.*
† "Interferenzialrefractor," *Cosmos*, 1856, No. 10, p. 227; and Pogg. *Ann.* vol. xcviii. pp. 345-349.

the application of the phenomena of interference in thick plates. A plate with parallel faces is cut into two parts. One of these, P_1, is fastened in a stand and receives a pencil of parallel rays.   A ray of light from A (fig. 1, Plate V.) is partly reflected upon the front face of plate P_1, and partly on the back one, and is thus divided into two pencils, which are delayed in regard the one to the other by the passage in the glass plate, and the loss of phase caused by the reflexion at the back surface.   At some distance, and in the path of the two parallel rays, the second half, P_2, of the glass plate is set up in a position parallel to the first one. Then the original ray (always apart from manifold internal re-flexions) is divided into four, two of which appear perfectly coin-cident both in phase and direction.   One of these two is the one which is reflected at the front surface of the first glass and at the back surface of the second glass; the other is reflected at the back surface of the first and at the front surface of the second glass (fig. 1).   In the intermediate space the two rays are sepa-rated by a distance which depends upon the thickness of the plates and their inclination to the rays, which can be increased at pleasure.   If P_1 and P_2 are the two parallel plates, we can imagine T and T_1 to be introduced media, and we can measure the displacement of the bands from B.   If, for instance, follow-ing Arago's proposition and Jamin's example, we introduce tubes of equal length containing liquids of different temperature, we can follow the alterations of the indices of refraction with great facility.   In this method certain difficulties are to be noticed: these consist, first, in the necessity for placing tubes of different temperature close to one another ; and secondly, that these tubes must remain of equal length, or that the alterations in their length must be taken into account.   This latter is very inconve-nient, while the required condition can scarcely be secured by mechanical means.   If, with Jamin, homogeneous instead of white light be employed, then, as Stokes* has pointed out, the results got from the displacements of the interference-fringes are somewhat too high, because, in consequence of the greater breadth of the band for rays of little refrangibility, the middle appears to be somewhat more displaced than it is in reality.

By this method Jamin obtained his above-mentioned determi-nations of the alteration with the temperature of the refractive index of water, and proved that the refractive index varied pro-portionally to external pressure†.

A method has often been brought forward for determining the index of refraction in liquids which is founded upon the measurement of the magnitude of the lateral parallel displace-

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* *Mémoires de l'Institut*, 1856, p. 453.
† *Ann. de Chim. et de Phys.* vol. lii. p. 163.

ment which a ray of light experiences in passing through a known thickness of a horizontal liquid layer. This experiment is performed by the observation of a mark at the bottom of a vessel before and after it is filled with a liquid.

Although it has been repeatedly shown that this method of determination is defective, and that a small error in the observation of the displacement gives rise to great differences, because great magnitudes are determined by small ones, yet of late recourse has been frequently had to various modifications of this plan*. Its value was stated to consist especially in the fact that the luminous ray can at once enter the exposed surface of the liquid from the air; while in investigating by means of prisms, alterations of the density may occur just at the important terminal surfaces. According to Poisson's view of capillarity, such a condensation must certainly take place at the surface of contact between the liquid and the glass; but such condensation would undoubtedly take place in layers parallel to the confining glass surface. It would vanish at a short distance from the glass, and the liquid would soon assume its normal density, so that the angle of refraction could not be affected by it. If, however, such an action of condensation were to take place within the range of observation, the image refracted (through a narrow hollow prism) of a long homogeneous straight line of light would necessarily appear convex; also a condensation of the liquid would take place towards the walls of the tubes. But I have never yet been able to detect anything of the kind, even on the passage of light through narrow metal tubes.

The method of refraction which has been chiefly used in the actual determinations of the index of refraction, and by means of which the excellent measurements of Fraunhofer[†] and Baden Powell[‡] were made, as well as those of Becquerel and Cahours[§], Deville[||], Delffs[¶], Dutirou[**], Beer and Kremers[††], Hoek[‡‡], Landolt[§§], Handel, Ad. Weiss and E. Weiss[||||], Gladstone and Dale[¶¶], Forthomme[***], and finally also my own, includes a

* " Mémoire sur la détermination des indices de réfraction," *Comptes Rendus*, vol. xxxix. pp. 27–29; and " Neue Methode den Brechungsindex von Flüssigkeiten zu messen, von Ch. Montigny," Pogg. *Ann.* vol. cxxiii.

† *Denkschriften der Münchener Akademie*, vol. v. pp. 1812–1815.
‡ *Ann. de Chim. et de Phys.* S. 3. vol. v. p. 129.   Pogg. *Ann.* vol. lxix.
§ *Comptes Rendus*, vol. vi. p. 867.   Also Pogg. *Ann.* vol. li. p. 267.
|| *Ann. de Chim. et de Phys.* S. 3. vol. v. p. 129.
¶ Pogg. *Ann.* vol. lxxxi. p. 470.
** *Ann. de Chim. et de Phys.* S. 3. vol. xxviii. p. 176.
†† Pogg. *Ann,* vol. ci.   ‡‡ Ibid. vol. cxii. p. 347.
§§ Ibid. vol. cxxiii.
|||| *Wiener Akademieberichte*, vols. xxv. xxxiii.
¶¶ Phil. Trans. 1858, pp. 887 &c. Also Pogg. *Ann.* vol. cviii. p. 632 &c.; and Phil. Trans. 1863, p. 317.
*** *Ann. de Chim. et de Phys.* vol. lx. p. 307.

considerable number of variables, and has certain advantages and disadvantages.

The most usual method is to take the minimum, and thence to derive the index of refraction from the formula

$$n = \frac{\sin \dfrac{\alpha + \delta}{2}}{\sin \dfrac{\alpha}{2}}$$

(if α be the angle of the prism and δ the least refraction). Another method, perhaps a little more exact, was first employed, as far as I am aware, for exact measurements by Seebeck, and consists in measuring the angle of the emergent as well as that of the incident ray. In the first place, this method requires, in order to avoid endless complication, that the prism be placed over the centre of the circle of the goniometrical instrument; it further necessitates the determination of very many angles, whereby its accuracy is partly forfeited. From this instrument, which Seebeck* had already described in 1830, Meyerstein's spectrometer and Babinet's goniometer, in its more perfect form (instruments used for similar purposes), were gradually developed. Van der Willigen used the first of these apparatus in his above-mentioned observations, while Babinet's goniometer was employed by Dutirou and the Vienna physicists Handel and Weiss, who, under Grailich's supervision, obtained the excellent results of their researches on the refractive indices of mixed liquids.

If the prisms are not in the centre (and it is impossible to place them there in theodolites and most goniometrical instruments), correction must be made for the excentric position of the prism. As it was important for me to be able to warm the prism at will, and to combine continual determinations of the refracting angle with measurements of the refraction, I chose the following plan and arrangement.

Use was made of the theodolite by Pistor and Martin, the telescope and vertical angle of which could be removed, and which stood in the Physical Cabinet in the University of Leipzig upon a solid stone cylinder about 1 metre in height. Upon this theodolite was placed a table with adjusting feet supporting on three points the hollow prism which held the liquids to be examined, and which could be moved on grooves in two directions at right angles to one another. At a distance of about 30 centimetres, a Repsold's " universal circle " was placed upon a firm wooden support, the bent telescope of which was at the same height as the hollow of the prism. At the same height as

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* *Observationes circa nexum intercedentem*, &c.   Inaugural Dissertation. Berlin, 1830.

these two telescopes, and at a distance of about 8 metres, a screen was placed which carried a moveable vertical slit, behind which the flame was afterwards placed. A little on one side of the prism a fixed telescope was placed upon a second wooden support, and so directed that by its means, on the one hand, the edge of the refracting angle of the prism could be fixed vertically, and, on the other, the angle of the prism could be determined by reflexion-observations.

Fig. 2 explains this arrangement. T is the theodolite, U the universal circle, P the prism, F the auxiliary telescope : S denotes the direction of the slit, and O the direction of the point of a distant lightning-conductor. The square border is intended to represent that the entire apparatus rests on one and the same stone basement. The following operations are necessary for the adjustment of the instrument :—

(1) Fixing the axis of rotation of the theodolite vertical by means of a level.

(2) Centring and fixing the hollow prism in such a manner that the line of intersection of the two including glass plates is parallel to the axis of revolution, and that the latter passes through the plane which bisects the angle of the prism. The first of these two conditions may be completely satisfied by shifting the prism by means of the adjusting screws of the supporting table until a distant object O, which lies in the same horizontal plane as the prism and the axis of the auxiliary telescope, is so mirrored on both sides of the prism that it appears by both reflexions on the horizontal thread of the auxiliary telescope. The second condition is only approximately satisfied.

(3) Placing the slit at the same height as the prism, and ensuring its verticalness by comparison with a plumbline.

(4) Fixing the universal circle.

The slit is first illuminated by as strong a light as possible, and the place is sought where the minimum refraction occurs. The universal circle is brought into this place, and its position is changed until the refracted spectral image of the slit is seen in the telescope. It is certainly somewhat troublesome to find this image at first; but when it is once found, the apparatus can be easily placed at the same height as the slit, and its axis of rotation may be made vertical without losing sight of the image. At starting I have often used the device of directing the telescope of the universal circle to the prism, bringing a light behind the eyepiece, and then fixing the slit at a distance of about 8 metres, when the refracted image of the light was seen. After this, the positions of slit and universal circle were more correctly adjusted. When the axis of the universal circle has been adjusted vertically by the level and the minimum of refraction

has been exactly determined, then the refracted image of the slit illuminated by the sodium-flame is brought to coincide with the vertical thread of the telescope. It is well known that at the minimum refraction the rays, on emerging, diverge in the same manner as if they had proceeded directly from the slit; so that, since the difference in the paths is very small, the slit may be seen directly and distinctly. If the instrument is accurately adjusted, the refracted and direct images of the slit must appear at the same height in the telescope. If the difference is considerable, the interval must be measured by means of the vertical circle, and the angular reading divided by the cosine of the difference in height.

The essential difference between the method adopted by me and that employed by Fraunhofer, Baden Powell, and others consists in the complete separation of my prism from the telescope, and its being placed upon a graduated circle so that its rotation can be measured. I chose this arrangement partly because I could thus warm the prism at will, and keep it warmed without altering its position, and finally because by this means I could introduce continual determinations of the refracting angle by means of reflexion-observations. Moreover this method is rather to be preferred to the others for measuring the alteration of the index of refraction with the temperature.

On altering the refractive power of the medium with which the hollow prism is filled, the angle of least refraction is changed. But since the telescope receives and collects parallel rays as long as any part of the light which leaves the prism falls within the cone which can be drawn from the eyepiece to the object-glass, it is clear that the refracted image of the slit can be included, even under great alterations of the angle of least refraction.

The observations divide themselves under two principal heads—the determination of the refractive angle of the prism, and the determination of the angle of least deviation.

(1) *The measurement of the angle of the prism.*—A prism being fastened to a graduated moveable circle (arranged as described), and an auxiliary telescope at the same level being directed to it, distant objects can be seen reflected on its surface. The angular determination is found simply from the difference of the readings on the graduated circle when one and the same distant object appears reflected on one or the other surface of the prism.

(2) *The determination of the angle of least deviation.*—By the arrangement adopted, the angle of least deviation is not directly measured upon the universal circle, but a correction must be introduced in the reading in consequence of the excentric position of the prism. If (fig. 3) S denotes the slit, P the prism, O the centre of the universal circle, and δ the angle of refrac-

tion, then

$$\delta = \phi + \psi,$$

and

$$\tan \psi = \frac{\overline{OP} \sin \phi}{\overline{OS} - \overline{OP} \cos \phi}.$$

In order to determine ψ, it is not only necessary to know ϕ (which is measured directly on the universal circle), but also the distance of the slit from the centre of that circle and its distance from the prism.

III. *The Instruments employed in the Investigation.*

(1) The theodolite served both as carrier for the prism and as reflexion goniometer. It is divided into sixths of a degree, and by help of the vernier allows a reading of $10''$. As two verniers were consulted, which stood at an angle of 180° from one another, any possible error of excentricity was thereby eliminated. That no serious errors occur in the graduation of the instrument is guaranteed partly by the name of the maker, and partly by the testing and use which the instrument underwent in the hands of Professor Hankel.

(2) The universal circle is provided with a bent telescope and a very exact level for adjusting its axis of rotation vertically. The graduation of the horizontal circle is by Repsold. The reading off degrees and sixths of a degree is made with an index and lens ; the reading of minutes and seconds by means of two microscopes. Divisions of $10''$ are read off directly, quantities of one second are estimated.

(3) The straight measurements were made by means of two mahogany rods divided into millimetres and provided with brass ends. Since we are here only concerned with relative lengths and the accuracy of the divisions was established, the rods could be used without correction.

The measurement of the lengths was effected thus :—the slit and the centre of the universal circle were plumbed down upon the stone basement, a thread was stretched between the two points so obtained in order to establish their rectilineal relation, and upon this line the measuring-rod was placed. It was more difficult to determine the distance of the prism from the axis of rotation of the universal circle. Since the prism is of considerable size, it might be doubtful from what point the distance should be measured. That point was chosen which was formed by the intersection of the axis of the telescope with the plane bisecting the angle of the prism. As my prism was provided with a little circular opening exactly in the middle for the introduction of a thermometer, I generally read off the measure at

the two sharp edges of the opening and took the mean (fig. 4). At all events, by this means greater accuracy is secured than was attained by Schmidt, who measured this distance from the axis of rotation to the face of the prism next to the telescope.

(4) *The hollow prism.*—Two conditions are necessary in regard to this : first, that it be easily and surely warmed ; and secondly, that it be kept at as constant a temperature as possible during the experiment.   I had the arrangement, at first, as follows :—A glass tube of about 2 centims. internal diameter, and 2 or three millims. thickness of glass, was ground smoothly at the ends in such a manner that the sides were inclined to one another at an angle of about 60°.   Exactly in the middle of this tube was a circular opening of about 1 centim. radius, into which another glass tube was cemented watertight for the reception of a thermometer.   The ground tube was placed in a prism-shaped sheet-metal box open above, and whose section was an equilateral triangle.   Through the side walls the glass tube projected about 1 millim., and was fitted and cemented as closely as possible into the box.   Upon the two flat glass edges were laid two plane glass plates which were taken from an old artificial horizon by Troughton, and which had been previously tested by means of reflexion in regard to their flatness and the parallelism of their faces.   By means of a brass diaphragm, which was fastened by three screws to the metallic box, the glass plates were pressed upon the tube by turning the screws. This entire box was placed in a second similar one, which was only so much greater than the first as to receive it without sticking or touching.   The second box had a triangular hole cut out of its bottom, so that a lamp standing on the theodolite could directly warm the bottom of the smaller prism.   The entire arrangement was closed by a cover which had only a small hole corresponding to the glass tube.   At the places where the introduced tube enters the inner box and is closed by the plates A, openings are formed in the outer box P_2 which can be closed by flaps K (fig. 5).   The liquid to be examined is introduced into the glass tube G ; and P_1 is filled with any other liquid.   A thermometer is introduced at R, its bulb reaching exactly into the middle of the glass tube G ; and it carries a cardboard screen immediately below the scale, in order to protect the projecting part of the scale from radiant heat.   The liquid under examination was surrounded by another liquid, in order to warm it more generally, and to avoid thereby quick and sudden changes of temperature.   The object of the external box was to diminish the outward radiation of heat by interposing a layer of air as a bad conductor.   In order to hinder the mobility of the air and to diminish the effect of upward currents, the intervening space

r was filled with very fine cotton-wool. The shutter K always remained closed until the commencement of the experiment, in order to diminish as much as possible the radiation of heat and the cooling of the glass plates.

When I began my measurements with the apparatus constructed in this manner, the inconvenience at once declared itself that, in order to maintain the flat glass plate tight up against the glass tube, it was necessary to screw the three screws very hard. In consequence of the great pressure to which the plates were thereby subjected, the images of Fraunhofer's lines at higher temperatures appeared indistinct, and the reflexion of distant objects showed either no images at all or only extremely indistinct and bleared ones, so that the desirable accuracy could not be attained in the angular measurements. When, however, finally, and with the greatest labour, a series of measurements had been taken, they showed such irregularities as to make it certain that a considerable source of error must be present. When, in consequence of this, the alteration in the prism by heat came to be examined by the scale and telescope, these alterations were not only found to be more considerable than was expected, but also to vary in no manner connected with the temperature.

The entire apparatus was taken to pieces; and the cause of these remarkable alterations in the angle was found to be owing to a mistake of the mechanician, who had allowed one of the glass plates to touch the brass of the box P_1. The defective reflexion arose from the glass plate, by projecting a little over the glass tube, and being fastened, as is shown, fig. 6, assuming a convex form when the pressure was increased. An entire re-arrangement of the apparatus became necessary; and the observations obtained, the result of several weeks' labour, had to be rejected. In place of the glass tube a brass one was employed, which was soldered into P, a brass collar being soldered on to P_1 at the place where the tube entered it. This brass was ground flat with extreme care, so that the flat glass plates only required to be pressed very gently in order to secure a perfectly water-tight joint. Upon the glass plates was laid a caoutchouc ring, and upon this a brass diaphragm, which was pressed very gently by means of the screws (fig. 7). In this manner not only was the joint tight, but every alteration in the form of the glass was avoided. In order to prevent the oxidation of the brass by the liquids introduced or by the air, the whole of the inside of the tube was strongly gilded. All the experiments were performed with this arrangement of the instrument, which proved itself a thoroughly good one.

It is true that slight alterations are shown in the angle with

increase of temperature, and also that a slight touching of the glass plates might cause such to take place, because the plates are connected to the tube with scarcely any friction. Accordingly, along with the measurements of the angle of least deviation, continuous measurements must also be made of the refracting angle of the prism. For this reason the arrangement of the instrument shown in fig. 2, Pl. V. was chosen.

The hollow prism itself showed by the most careful testing absolutely no proper refraction, so that it was not necessary to apply any correction on this account*.

(5) The thermometer used for measuring the temperature in the inside of the prism was a little one by Greiner (Réaumur, with paper scale) divided from $-55°$ to $80°$. It was possible to judge to one-tenth of a degree, without, however, being sure of the accuracy to two-tenths of a degree, since the thermometer had often to be read very rapidly, and the degrees were not quite 1 millim. apart. Only the lower part of the thermometer dipped into the liquid. From $-55°$ it was below the sheet of cardboard, by which it was protected from the heat radiated or convected from the prism or the lamp beneath. It was necessary, therefore, to correct for the projecting portion of the scale; and for this purpose the formula given by Kopp was employed,

$$T = \tau + v \cdot \alpha(\tau - t),$$

where τ is the temperature read off, t the temperature of the scale, α the apparent coefficient of expansion of mercury in glass ($0·000154$), and v the number of degrees in the projecting part†.

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* A formula of correction for this purpose is found in Biot, *Précis Élémentaire de Physique Expérimentale*, 1842, vol. ii. p. 113.

† As I have nowhere found a derivation of this formula, I may be permitted to give it shortly here. Let t be the temperature of the air, T that of the liquid, τ the temperature read off, v the number of degrees not immersed, V the volume of mercury in the thermometer at zero, the space between two degrees being taken as unity, V the volume of the immersed part reduced to zero, v the number of degrees representing the volume not immersed. Then

$$\frac{v}{1+at} + V = V, \quad . \quad . \quad (1) \qquad 1 + \alpha \cdot 100 - V = 100, \quad . \quad . \quad (2)$$

$$V = \frac{1}{\alpha} - V(1 - \alpha t), \quad . \quad (3) \qquad V = \frac{1}{\alpha}; \quad . \quad . \quad . \quad . \quad (4)$$

further, we have $\qquad v + V(1 + \alpha T) = V(1 + \alpha \tau),$

because a reading τ corresponds to a state as if V had become $V(1+\alpha\tau)$. Hence from (3) and (4), putting in V and V,

$$T = \tau + v\alpha(T - t).$$

For a first approximation $T = \tau$, and T_1 is thus found. This is substituted for T, and thus T_2 is got, and so on. In most cases a first approximation is sufficient.

Further, the temperatures were compared with an excellent normal thermometer by Greiner, divided into half degrees, belonging to Professor Hankel, and which was properly corrected. The comparison gave:—

I. Reading on the normal thermometer. II. Simultaneous reading on the thermometer employed in the experiments.

I.	II.	Δ.	I.	II.	Δ.	I.	II.	Δ.
80·0	79·5	5	40·5	40·0	5	19·4	19·0	4
69·8	69·4	4	36·7	36·2	5	16·8	16·5	3
68·5	68·1	4	30·5	30·2	3	10·0	10·0	0
66·7	66·2	5	30·4	29·9	5	8·7	8·5	2
65·6	65·0	6	27·2	26·4	8	7·2	7·0	2
64·8	64·2	6	27·0	26·2	8	5·9	5·8	1
60·1	59·4	7	26·8	26·0	8	4·0	4·0	0
57·3	56·4	9	24·4	23·9	5	3·6	3·4	2
54·8	54·2	6	23·7	23·1	6	3·1	3·1	0
52·6	52·1	5	23·2	22·7	5	2·8	2·8	0
50·5	50·0	5	21·7	21·2	5	1·6	1·6	0
48·7	48·3	4	18·5	18·0	5	0·0	0·0	0
43·8	43·4	4						

Hence the following corrections are deduced:—

80° 65° 60° 55° 50° 35° 30° 25° 20° 15° 10° 5° 0°

0°·5 0°·6 0°·7 0°·6 0°·5 0°·6 0°·7 0°·6 0°·5 0°·4 0°·2 0°

(6) *The slit.*—In order to obtain a straight line of light, an ordinary moveable interference-slit was employed, the two edges of which were about $\frac{1}{2}$ a millimetre apart. This was so fastened to a holder on a screen as to be moveable in two directions at right angles to one another.

(7) *The source of light.*—The choice of the source of light also demanded much consideration and many experiments. It would have been best, in order to come to a clear conclusion about the alteration of the refraction with the temperature, to have used sunlight, and to have taken Fraunhofer's lines as the fixed data. As, however, I made my experiments in winter, and as considerable time was necessary for each one of them, I was obliged to dispense with this light, because in our climate the sun is very often invisible for weeks together, and I did not choose to be so dependent upon the weather. Fraunhofer's lines in diffused daylight, even when a condensing-apparatus is used, are so feeble that they could not be employed. I contemplated next making use of the absorption spectra of gases, such, for instance, as nitrous acid, which Hankel, Grailich, and Weiss had used in their experiments. The coincidence of some of their

lines with Fraunhofer's has been proved by Grailich[*]. A later observation of A. Weiss has shown that, on altering the temperature or density of the vapours, displacements occur in the lines in such a way that some of them disappear and new ones are formed. The method is also not much to be recommended, because on employing artificial light, the more refrangible part of the spectrum beyond F contains too few rays. To procure another sort of homogeneous light, such as Fraunhofer suggested and Dutirou[†] employed, requires rather a complicated arrangement. The reader is therefore referred to the original communication.

The simplest means which appeared to me to remain was to make use of the bright lines which appear in the spectrum-apparatus caused by the flames of incandescent metals. The sodium-line appeared at once for the Fraunhofer line D. All other metals, such as potassium, strontium, calcium, &c., gave lines which were too weak to be seen at a distance of 8 metres by means of my best telescope; so that there only remained the red lithium- and the green thallium-line. The brilliant lines of cæsium, indium, and other newly discovered metals could not be employed, on account of the dearness of their preparations.

The three lines of hydrogen gas incandescent in the induction-current of a Ruhmkorff's coil passing through a Geissler's tube, such as Landolt used, could not be employed, on account of practical difficulties.

As in calculating the formula of dispersion it was necessary to know the undular length of the homogeneous light, an attempt was made to estimate this quantity under the hypothesis that the undular length for the line D ($\Lambda_D = 0 \cdot 0005888$ millim.) was known. I made use of a Fraunhofer's lattice, and measured the distance of the first refraction-images from one another. According to the theory of the refraction-spectrum, the sines of the angle of deviation must be proportional to the lengths of the waves. Unfortunately it was not possible to measure exactly to less than $10''$ with the theodolite. Moreover it was rather difficult to catch the feeble lithium-light line, and the only momentarily appearing line of the volatile thallium. The measurements obtained are the following :—

Lithium-line.				Sodium-line.				Thallium-line.			
°	′	″	Δ	°	′	″	Δ	°	′	″	Δ
1	50	55	−6	1	37	15	+ 1	1	28	8	+13
1	50	45	+4	1	37	17	− 1	1	28	25	− 4
1	50	47	+2	1	37	18	− 2	1	28	25	− 4
1	50	43	+6	1	37	15	+11	1	28	27	− 6
1	50	48	+1	1	37	18	− 2	1	28	18	+ 3
1	50	57	−8	1	37	22	− 6	1	28	22	− 1
1	50	49	mean	1	37	16	mean	1	28	21	mean

[*] *Krystallograph. opt. Untersuchungen*, p. 21.
[†] *Ann. de Chim. et de Phys.* S. 3. vol. xxviii. p. 186.

We have the continuous proportion

$$\Lambda_{Li} : \Lambda_D : \Lambda_{Th} = \sin 1° \, 50' \, 49'' : \sin 1° \, 37' \, 16'' : \sin 1° \, 28' \, 21''.$$

Since now Λ_D is known, we thence get

$$\Lambda_{Li} = 0 \cdot 0006708, \quad \Lambda_{Th} = 0 \cdot 0005348.$$

If, further, we remember that, according to Fraunhofer's measurements*,

$$\left. \begin{array}{l} \Lambda_B = 0 \cdot 0006878 \\ \Lambda_C = 0 \cdot 0006564 \end{array} \right\} \; \Lambda_{Li} = 0 \cdot 0006708,$$

$$\left. \begin{array}{l} \Lambda_D = 0 \cdot 0005888 \\ \Lambda_E = 0 \cdot 0004843 \end{array} \right\} \; \Lambda_{Th} = 0 \cdot 0005348,$$

we see that the red band of lithium falls between B and C, and that the homogeneous green light of thallium falls between the Fraunhofer's lines D and E and very near to E.

The only other data known to me for these numbers are, first, one by Fizeau† for red lithium light derived from phenomena of interference of another kind, $\Lambda = 0 \cdot 0006703$; secondly, measurements by Müller‡ in Freiburg, made according to the method I employed. These gave

$$\Lambda_{Li} = 0 \cdot 0006763, \quad \Lambda_D = 0 \cdot 0005918, \quad \Lambda_{Th} = 0 \cdot 0005348.$$

The instrument used by Müller, a Babinet's goniometer, only allowed readings to one minute. As Fraunhofer's numbers, although not trustworthy in the fourth decimal place, are nevertheless the most exact, I attach the greatest value to my determinations of the undular length of the lithium- and thallium-lines which rest upon these data. The most probable errors, w, of the final result of my observations are

$$w = \pm 0 \cdot 6745 \sqrt{\frac{\Lambda_1{}^2 + \Lambda_2{}^2 + \Lambda_3{}^2 + \cdots}{s(s-1)}},$$

$$w_{Li} = 1'' \cdot 5, \quad w_{Na} = 1'' \cdot 6, \quad w_{Th} = 1'' \cdot 9,$$

from which the accuracy of my results may be estimated.

[To be continued.]

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* Denkschrift der Münchener Akademie aus dem Jahre 1823. Gilbert's *Annalen*, vol. lxxviii.

† *Loc. cit. Ann. de Chim. et de Phys.* S. 3. vol. lxvi. p. 429. I may be allowed here to draw attention to a trifling error of Fizeau. This physicist considers the yellow line of lithium β_{Li} to be identical with the sodium-line. That this is not the case is shown by Kirchhoff's data as well as by simple inspection.

‡ Pogg. *Ann.* vol. cxxviii. pp. 642–644.

XXXI. *On the Direct Transformation of Chloriodide of Ethylene into Glycol.* By Maxwell Simpson, *M.D., F.R.S.*[*]

SOME years ago[†] I discovered a compound having the composition $C^2 H^{4\prime\prime} \begin{cases} Cl \\ I \end{cases}$, which I called chloriodide of ethylene. With this body I have tried a great many experiments, in the hope of being able, whilst retaining one of the metalloids in its place, to substitute a monatomic radical, such as hydroxyl, cyanogen, &c., for the other. These experiments have all failed. I have found that the metalloids in this compound always act in concert, so that it is impossible to replace one of them by any radical without at the same time replacing the other. One of these experiments I will now describe, as it produced a definite result.

In the hope of forming a chloralcohol, I heated one molecule of the chloriodide of ethylene with one molecule of moist oxide of silver, expecting that the reaction would take place according to the following equation:—

$$C^2 H^{4\prime\prime} \left\{ \begin{matrix} Cl \\ I \end{matrix} + \begin{matrix} Ag \\ H \end{matrix} \right\} O = C^2 H^4 Cl . O H + AgI.$$
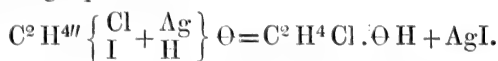
My expectations, however, were not realized. Instead of a chloralcohol I obtained ethylglycol as the product of the reaction, both the metalloids having been replaced by hydroxyl:—
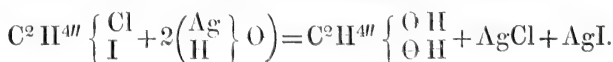
$$C^2 H^{4\prime\prime} \left\{ \begin{matrix} Cl \\ I \end{matrix} + 2 \left(\begin{matrix} Ag \\ H \end{matrix} \right\} O \right) = C^2 H^{4\prime\prime} \left\{ \begin{matrix} O H \\ O H \end{matrix} + AgCl + AgI. \right.$$
<center>Glycol.</center>

The experiment was performed in the following manner:—Into a strong glass matrass with a long neck I introduced one molecule of the chloriodide and one molecule of moist oxide of silver. I then sealed the matrass and exposed it for twenty-four hours to a temperature ranging between 160° and 200° C. At the expiration of this time I opened the matrass and filtered its contents. The filtered liquor, which was perfectly transparent and colourless, was then subjected to distillation. As soon as the water had passed over, the thermometer rose rapidly to 180° C.; and between that temperature and 220° C. a considerable quantity of a syrupy liquid distilled over, which I recognized to be glycol by the following properties:—It had a sweet taste, it was soluble in water, it boiled between 195° and 200° C., and gave, when treated with hydriodic acid, iodide of ethylene. The same results were obtained when one molecule of the chlor-

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iodide was subjected to the action of *two* molecules of the hydrated oxide of silver.

In distilling the product of the foregoing reaction, I observed that a small quantity of hydrochloric acid passed over after the water. The production of this acid I could not account for except by supposing that the chloriodide decomposed the water which was present, as well as the oxide of silver (of which there was only one molecule), and that both reactions gave the same product. The following equation will make this intelligible:—

$$C^2\,H^{4\prime\prime} \left\{ \begin{matrix} Cl \\ I \end{matrix} \right. +2\left(\begin{matrix} Ag \\ H \end{matrix} \right) \Theta \right\} = C^2\,H^{4\prime\prime} \left\{ \begin{matrix} \Theta\,H \\ \Theta\,H \end{matrix} \right. + AgCl + AgI,$$

$$C^2\,H^{4\prime\prime} \left\{ \begin{matrix} Cl \\ I \end{matrix} \right. +2\left(\begin{matrix} H \\ H \end{matrix} \right) \Theta \right\} = C^2\,H^{4\prime\prime} \left\{ \begin{matrix} \Theta\,H \\ \Theta\,H \end{matrix} \right. + HCl + HI.$$
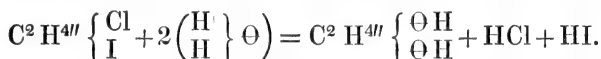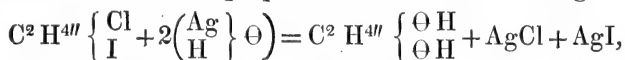
In order to determine this point I exposed one part by weight of the chloriodide and five parts by weight of distilled water, in a sealed tube, to a temperature ranging between 160° and 220° C. till all the chloriodide had disappeared. I then opened the tube and neutralized the product (which contained hydrochloric and hydriodic acids coloured with a little free iodine) with dilute potash. On subjecting this to distillation I obtained a syrupy liquid as before, which passed over between 180° and 220° C., and had all the characters of glycol. The quantity obtained was small, a portion of it having been converted into iodide of ethylene by the hydriodic acid formed in the reaction.

XXXII. *Note of Experiments upon the Conduction of Heat by Liquids. By* FREDERICK GUTHRIE, *Ph.D., F.R.S.E., Professor of Physics and Chemistry, Royal College, Mauritius*[*].

IN the numerous and excellent studies which have been made of conductivity, the attention of physicists has been hitherto mainly directed to solids. Yet it must be admitted that, in regard to their conductive powers, as well as in their other thermal relations, gases and liquids present both theoretically and practically many points of preeminent interest.

No solid body can be said to be without structure. Definite chemical compounds in the solid form, notoriously and perhaps without exception possess crystalline form. Even such bodies, simple or complex, as appear without crystalline form (that is, which are amorphous) are nevertheless not without structure. They show, on fracture, surfaces of least resistance; and though these surfaces may be so irregular as to defy mathematical formulization, they yet prove that the cohesion is not uniform—that

* Communicated by the Author.

is, that the contiguous parts of the body do not stand in identically the same mechanical relation to one another throughout. Even two specimens of the same solid substance, alike in all other respects, are probably never identical as to internal arrangement. The solids the most homogeneous with regard to structure are undoubtedly those which have been derived from the liquid state, either by cooling after fusion or by deposition from solution. But as the physical conditions attending either of these processes of solidification are never strictly uniform, we cannot suppose that the result should be precisely similar in different instances.

Still less uniformity, of course, must be expected where the solid is the result of organic forces. Structure is here complicated to the highest degree. Not only do different specimens of a substance differ from one another, but the structure of one and the same specimen is not alike throughout.

Dr. J. Tyndall has shown that cubes of wood possess different conducting-powers for heat, according as the heat has to travel parallel to the axis of the tree, in a radial, or in a tangental direction. This difference is undoubtedly due to the prevailing cylindrical structure of the layers of which the wood is formed. For if the tree's stem be supposed to be formed of concentric cylinders of alternately harder and softer material, and if the harder substance conduct heat better than the softer, it might be foreseen that the greatest conduction will take place parallel to the axis of the tree, the least radially, and that the conducting-power in a tangental direction will depend upon the distance from the tree's axis at which the cube is taken.

Axial.   Radial.   Tangental.
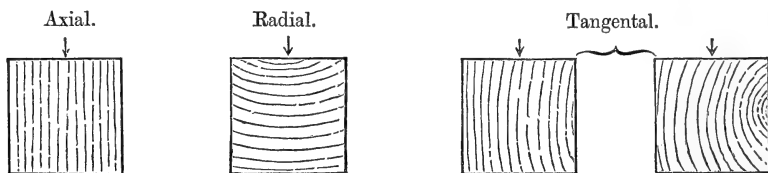
Though less obvious, somewhat similar differences must exist in different specimens of other solid substances. Thus we should expect pure iron to show different conducting-powers, according as it is simply solidified on cooling, or welded or rolled. For in the former case it possesses a crystalline, in the second a fibrous, and in the third a laminar structure.

Gases and liquids, on the other hand, are essentially without structure, and they accordingly offer the most tempting ground for the examination of conduction. Two cubic inches of water are physically so thoroughly identical, that deductions drawn from the behaviour of the one, under given influences, most as-

suredly are true of the other. The same identity may be predicated with even greater safety of vapours and permanent gases.

Magnus has endeavoured to show that hydrogen has a specific and preeminent conducting-power.

The examination of the conducting-powers of liquids is mainly due to Rumford, Murray, and Despretz.

The well-known experiment of Rumford, in which water is boiled over ice, led that experimentalist to conclude that water does not conduct heat.

Murray placed the bulb of a thermometer under a layer of oil or mercury in a hollow cylinder of ice, and applied heat from above. He concluded that both liquids conducted heat, and that mercury did so more readily than water.

Despretz* enclosed water in a wooden cylinder painted internally and placed thermometers down the axis of the cylinder. He heated the upper surface of the water-column by means of a copper vessel into which fresh portions of hot water were continually poured. After several hours (thirty or sixty) he obtained a state of thermal equilibrium. Despretz concluded that in water the temperatures of successive points of the axis of the cylinder equally distant from one another are in geometrical progression, and that accordingly the same law obtains with liquids as with solids. The same observer also concluded that salt dissolved in the water does not sensibly affect its conducting-power. Though Despretz inserted thermometers in the wooden walls of his cylinder, and placed some also excentrically in the water-column, and deduced that the column diminished in temperature from the axis outwards and that the walls were cooler than the column, yet, in such experiments, it is difficult to admit that the conducting-power of the containing vessel, be it greater or less than that of the water, is without influence. Further, while the dimensions chosen by Despretz for the liquid column (1 metre high, 405 millims. in diameter) are inadmissible for many liquids, the thermometer-bulbs would interfere with the thermal manifestations in smaller columns.

In order to compare the conducting-powers of different liquids with one another, and to measure approximately the absolute conducting-power of one liquid, two conditions appear essential. The liquid must be heated from above; it must not be heated in a vessel whose sides conduct with anything like the power which the liquid enjoys. If the first of these conditions be neglected, phenomena of convection directly intervene; if the second, such vitiating phenomena are brought about by the conduction by the solid body.

* *Ann. de Chim. et de Phys.* vol. lxxi. p. 206 (1839). *Comptes Rendus,* vol. xxxiv. p. 540 (1852).

The accompanying figure shows the apparatus which I have employed for showing, comparing, and approximately measuring the conducting-powers of various liquids.

A and B are two conical copper bottles having very thin and perfectly flat bottoms of exactly the same size. The two vessels are fixed so that their flat surfaces are perfectly horizontal and at a little distance (say two or three millimetres) from one another. The liquid under examination is introduced, by a pipette, between the two surfaces at W, where it remains, supported by adhesion. The neck of the vessel A is fitted with two tubes like those of a washbottle. The lower vessel B serves as an air-thermometer, its neck carrying a tube T which dips into a reservoir of water R. Steam, or a current of warm water, is passed through the vessel A. By this means its lower surface is raised to and maintained at a uniform temperature. It is clear that as the liquid W can only be heated from above, and as there are no walls to the conducting column, any expansion which is shown by the depression of the water in T must arise from true conduction.
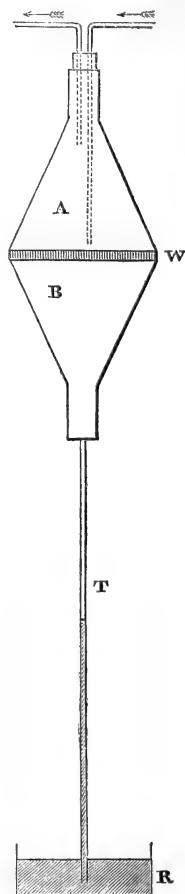
It may be asserted that there is in all cases a radiation through the liquid. If there be a specific radiation independent of media, it will clearly be a constant which may be subtracted from the true conduction, and will therefore not alter the order of conductive power. If there be a radiation peculiar to each medium, its manifestation may be fairly included in the phenomena of conduction; for atom-to-atom radiation is no other than conduction proper.

Two methods of measurement may be employed :—

(1) The time necessary for the production of a given expansion.

(2) The expansion produced in a given time.

Subjoined are the numbers derived from a preliminary series of experiments. They show, in millimetres, the depression produced in the tube T when A is maintained for one minute at a given temperature above that of the air. These numbers have accordingly at present no absolute positive value. To have this,

it is obvious that many other data must be taken into account. These are notably the thickness of the layer of liquid at W, the capacity for heat of the various liquids, the relative volumes of the vessel B and its tube, &c.

Arranged in the order of quantity of heat conducted, it appears from these experiments that the following bodies are in the following order :—

Mercury	333
Water	270
Oil of turpentine	230
Glycerine	216
Iodide of amyl	200
Nitrobenzol	170 ⎫
Aniline	170 ⎭

On obtaining these well-marked differences, innumerable suggestions at once offered themselves—such as the employment of a thermoelectric pile in place of the air-thermometer. And some of the results gathered from this prolific field I propose to communicate subsequently.

London Institution,
  March 16, 1868.

XXXIII. *On* Mr. C. F. Varley's *Reciprocal Electrophorus.* *By* Sir WILLIAM THOMSON, *LL.D., F.R.S.**

HAVING been informed by Mr. Fleeming Jenkin that he had heard from Mr. Clerk Maxwell that the instrument which I described under the name "Replenisher," in the Philosophical Magazine for January 1868, was founded on precisely the same principle as an instrument "for generating electricity" which had been patented some years ago by Mr. C. F. Varley, I was surprised; for I remembered his inductive machine which had been so much admired at the Exhibition of 1862, and which certainly did not contain the peculiar principle of the "Replenisher." But I took the earliest opportunity of looking into Mr. Varley's patent (1860), and found, as was to be expected, that Mr. Maxwell was perfectly right. In that patent Mr. Varley describes an instrument agreeing in almost every detail with the general description of the "Replenisher" which I gave in the article of the Philosophical Magazine already referred to. The only essential difference is that no contacts are made in Mr. Varley's instrument, but, instead, the carriers pass, each at four points of its circular path, within such short distances of four

metallic pieces that when a sufficient intensity of charge has been reached, sparks pass across the air-intervals. Hence to give a commencement of action to Mr. Varley's instrument, one of the inductors must be charged from an independent source to a considerable potential (that of several thousand cells for instance), to make sure that sparks will pass between the carriers and the metal piece (corresponding to one of my connecting springs) which it passes under the influence of that inductor. In my " Replenisher," however well discharged it may be to begin with, electrification enough is reached after a few seconds (on the compound-interest principle, with an infinitesimal capital to begin with) to produce sparks and flashes in various parts of my instrument. In Mr. Varley's instrument, what corresponds to my connector is described as being connected with the ground; and the effect is to produce positive and negative electrification of the two inductors. In this respect it agrees with the self-acting apparatus for multiplying and maintaining electric charges, described in a communication to the Royal Society last May*. From this arrangement I passed to the " Replenisher " by using a wheel with carriers as a substitute for the water-droppers, and arranging that the connectors might be insulated and one of the inductors connected with the earth, which, of course, may be done in Mr. Varley's instrument, and which renders it identical with mine, with the exception of the difference of spring-contacts instead of sparks. This difference is essential for some of the applications of the " Replenisher," which I described, and have found very useful, especially the small internal replenisher, for replenishing, when needed, the charges of the Leyden jar of my heterostatic electrometers. But the reciprocal-electrophorus principle, which seemed to me a novelty in the communication to the Royal Society and in the Philosophical Magazine article of last January referred to, had, as I now find, been invented and published by Mr. Varley long before, in his patent of 1860, when it was, I believe, really new to science.

Postscript.

Glasgow College, March 20, 1868.—In looking further into Mr. Varley's patent, I find that he describes an arrangement for making spring-contacts instead of the narrow air-spaces for sparks,—and that he uses the spring-contacts to enable him to commence with a very small difference of potentials, and to magnify on the compound-interest principle. He even states that he can commence with such a difference of potentials as can

* Proceedings of the Royal Society, 1867; or Phil. Mag. November 1867.

be produced by a single thermoelectric element, and by the use of his inductive instrument can multiply this in a measured proportion until he reaches a difference of potentials measurable by an ordinary electrometer. Thus it appears that his anticipation of all that 1 have done in my "Replenisher" is even more complete than I supposed when writing the preceding.

XXXIV. *Electrolytic Investigations.* By M. P. A. FAVRE*.

I HAVE the honour of communicating to the Academy the continuation of my thermal investigations on the battery considered as a decomposing agent. I hope that the new results I am about to communicate will give an idea of what may be expected from attempts in this direction to elucidate the chemical and dynamical theory of the battery, and that they will show that the calorimeter, which has already been of such use in chemistry, is destined to render even greater service. Let me hope that these investigations will foreshadow the future in store for thermal chemistry, which is now only in its infancy. I hope to contribute to demonstrate how important is the part the battery plays in the study of molecular work—a study so little advanced, and which, better known, will give a more accurate idea of the constitution of bodies, and of their mode of acting on each other.

For if the balance (which in the hands of Lavoisier and his successors has served to create modern chemistry, by determining the relative weights of bodies which act on each other) is indispensable to chemists, the calorimeter is no less so : it measures, weighs, so to say, the force set at work in chemical reactions, and gives a thermodynamic expression for the formation of bodies. The same is the case with the battery, which in these reactions, almost always complicated, enables us to follow and measure the distribution of the motive force which it developes.

I have already described the apparatus by means of which I measure the distribution of the motive force developed by the battery employed as an agent of chemical separation ; I will content myself with simply mentioning its principal parts.

The first mercurial calorimeter (*thermomètre à calories*) has seven muffles, and measures the heat remaining in the battery which it contains. This battery consists of five equal couples (*amalgamated zinc and platinum*), which are immersed in sulphuric acid suitably diluted. It occupies five muffles.

The physical resistance of the battery and of the interpolar, which includes the tangent-compass, is equal to about 50 millims. of my normal platinum wire. I have endeavoured to eliminate this

* Translated from the *Comptes Rendus,* February 10, 1868.

resistance, as well as the resistance of the same kind of the volta-meter which forms part of the interpolar, by interposing rheostats whose resistance expressed in platinum wire is 5000 to 6000 mil-lims. These rheostats are fitted in a test-tube full of water and placed in the sixth muffle of the calorimeter; so that all the heat transported and consumed outside the calorimeter might by ap-proximation be considered to be merely consumed in the electro-lysis of the body.

A second mercury calorimeter measures the heat disengaged in that part of the circuit placed outside the calorimeter which contains the battery and the rheostat. For this purpose each of the voltameters successively introduced into the voltaic circuit is placed in one of the muffles.

The first calorimeter estimates the heat which is borrowed from the battery for electrolyzing the bodies.

The second calorimeter indicates that amount of heat, thus borrowed from the battery, which after being used for electrolysis is restored by the elements set at liberty, when, immediately after chemical separation, and in virtue of an essentially local phenomenon, these elements become modified in passing from the *nascent state* (in which they exist in compounds) into the *ordinary condition.*

It is clear that the investigation of the distribution of heat in the voltaic circuit may require the use of a great number of ca-lorimeters.

I mention also that, excepting in the nature of the plates, the voltameters, both in their shape and in their dimensions, and in the distance of the plates, are just like the couples of the bat-tery, and the electrolytes are employed in such conditions that the same volume of water always contains quantities which are chemically equivalent to the quantity of sulphuric acid contained in the battery.

In the calorimeter which already contains the battery and the rheostat, and in the seventh muffle, the voltameter which forms part of the interpolar can be placed. In this case one and the same calorimeter contains the whole of the circuit.

I had already previously attempted to transfer to the inter-polar almost all the heat developed in a Smee's element, or in a battery composed of two or more Smee's elements of equal size. To obtain this result, I introduced into the interpolar, and out-side the calorimeter which contains the pile, as much as 700 millims. of *normal* platinum wire coiled on the cylinder of a rheostat specially arranged for this purpose. This resistance enables us to neglect almost entirely the physical resistance of the battery and of the interpolar arc which includes the boussole, seeing that this resistance, expressed as a length of wire, is only

about 50 millims. I may, however, mention that, working under these conditions, I could never transfer outside the battery more than about three-quarters of the heat it developes. A quantity representing about 6000 units remains obstinately confined there. It is this unexpected result which, after having long engaged my attention, has directed my researches in their present path, having led me to suspect the existence of secondary phenomena which render the reactions complicated.

Experiments.

Let us consider the following numbers furnished by the reaction of sulphuric acid and of sulphate of copper on various metals :—

<div style="text-align:right">Thermal
units.</div>

I. One equiv. of zinc, in replacing 1 equiv. of hydrogen in $SO^4 H$, gives . . . . } 19834

One equiv. of zinc, in replacing 1 equiv. of copper in $SO^4 Cu$, gives . . . . } 27346

One equiv. of iron   ,,   ,,   19025

  ,,   cadmium   ,,   ,,   16265

II. We are led to conclude that

If the metalloid radical SO^4, in combining with H, gives . . . . . . } x Thermal units.

in combining with   Zn it gives $x + 19834$

    ,,   ,,   Fe   ,, $x + 19025 - 7512$

    ,,   ,,   Cd   ,, $x + 16265 - 7512$

    ,,   ,,   Cu   ,, $x - 7512$

If we take as the value of x the heat corresponding to the formation of another sulphate (sulphate of copper for instance), we shall conclude—

III. That the radical SO^4, in combining with Cu, giving x,

the radical SO^4, in combining with Zn, should give $x + 27346$

    ,,   ,,   ,,   Fe   ,, $x + 19025$

    ,,   ,,   ,,   Cd   ,, $x + 16265$

    ,,   ,,   ,,   H   ,, $x + 7512$

It will be sufficient, then, to find the value of x to calculate the heat of formation of the other sulphates.

It is better to choose the value of x by referring it to the formation of sulphate of copper rather than of sulphate of hydrogen, because, in the decomposition of the latter sulphate, the thermal phenomenon due to the metal H set at liberty, and which passes from the *nascent* to the *ordinary* state, is exhibited in a much more pronounced manner than in the case of the other metals.

The value of x, thus referred to sulphate of copper, is obtained by examining the amount of heat which the sulphate of copper borrows from the pile during its decomposition in a voltameter with platinum plates placed outside the calorimeter which contains the pile and a rheostat offering sufficient resistance.

This quantity is 38950 thermal units (IV.).

Replacing x by its value, Table III. gives

			Thermal units.
V.	$SO^4 + Cu$	$=$	38950
	$SO^4 + Zn$	$=$	66296
	$SO^4 + Fe$	$=$	57975
	$SO^4 + Cd$	$=$	55215
	$SO^4 + H$	$=$	46462

In making a *thermal analysis* of other salts* (that is, decomposing them in the same manner as sulphate of copper), I obtained the quantities mentioned in the following Table:—

			Thermal units.
VI.	$SO^4 + Cu$	$=$	38950
	$SO^4 + Zn$	$=$	66040
	$SO^4 + Cd$	$=$	54470
	$SO^4 + H$	$=$	52242

which refer to the separation of the constituent elements of the salts in the condition in which they exist in their combinations.

The first three numbers, which are the direct result of experiment, agree in a satisfactory manner with those of the preceding Table (V.), which have been calculated on the basis of the result obtained by the electrolysis of sulphate of copper alone. The number referring to sulphate of hydrogen is the single exception, and the interpretation of this result is by no means the least interesting.

If to the quantity of heat disengaged during the formation of the following oxides by means of ordinary oxygen,

			Thermal units.
VII.	$Zn + O$	$=$	41992
	$Fe + O$	$=$	35103
	$Cd + O$	$=$	28925
	$Cu + O$	$=$	18055
	$H + O$	$=$	34462

we add the quantity of heat disengaged during the combination of these anhydrous oxides (oxide of iron excepted) with dilute sulphuric acid,

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* I except sulphate of iron, the electrolysis of which offers difficulties which have led me to defer its study.

Thermal units.

VIII.

$$SO^4 H + ZnO = 12304$$
$$SO^4 H + FeO = 10872*$$
$$SO^4 H + CdO = 14290$$
$$SO^4 H + CuO = 8895$$
$$SO^4 H + HO = 0$$

we effect the thermal analysis of the sulphates of zinc, iron, cadmium, copper, and hydrogen, by combining their constituent elements taken in the ordinary state, and we obtain the following numbers:—

Thermal units.

IX. Oxidation of zinc and conversion of its oxide into sulphate . . . . } 54296

Oxidation of iron   ,,   ,,   45975

,,   cadmium   ,,   ,,   43415

,,   copper   ,,   ,,   26950

,,   hydrogen   ,,   ,,   34462

These numbers are each about 12000 thermal units less than those of Table V. and of Table VI., with the exception of the number for hydrogen in Table VI., from which the difference is about 18000.

When the voltameter in which the sulphates are decomposed is placed inside the seventh muffle of the calorimeter in which is the battery, instead of being quite outside and apart from it, the following numbers are obtained:—

X.   Electrolysis of sulphate of copper . 26568

         ,,   ,,   hydrogen. 34204

numbers which do not much differ from those in the preceding Table (IX.), but which differ greatly from the numbers in Table VI. which refer also to the electrolysis of sulphate of copper and of sulphate of hydrogen.

If, changing the conditions of the preceding experiment, the voltameter, instead of being placed in the calorimeter in which is the battery, is placed in an independent one, numbers are obtained which explain the difference mentioned between the results of experiment VI. and those of experiments X.

The following are the numbers:—

	Heat taken from the pile and indicated by the calorimeter No. 1, which contains the pile and the rheostat.	Heat restored to the calorimeter No. 2, which contains the voltameter, by the elements of the salts decomposed.
XI. Electrolysis of sulphate of copper	38530	12445
,, ,, hydrogen	54235	20335

In these experiments (XI.) the heat disengaged in the volta-

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* *Annales de Chimie et de Physique,* vol. xxxvii. p. 405.

meter is indicated by the special calorimeter which contains it, while in experiments X. this heat is developed in the calorimeter of the battery itself, and is necessarily added to the quantity of heat which expresses the work consumed there.

That is the reason why there is restored to the calorimeter No. 2 a quantity of heat so considerable borrowed from the pile—heat the origin of which cannot be attributed to the physical resistance of the voltameter; for this may be almost neglected, since a rheostat presenting an adequate resistance has been introduced into one of the muffles of the calorimeter in which is the battery.

To what are we to attribute the very discrepant results in experiments VI., IX., and X. when the conditions are varied in which bodies of the same name are associated or dissociated?

This I shall more fully discuss in a more extended memoir; and I will restrict myself to giving the conclusions in a subsequent part of this paper. I will merely mention here that the cause of these differences is to be sought in the particular condition of the bodies (oxygen, hydrogen, &c.) concerned in the action, and which are considered sometimes in the *nascent* and sometimes in the *ordinary* state.

In the experiments in which a quantity of heat sufficient to decompose an equivalent of sulphate of zinc in a voltameter is brought into play, I was not long before I saw that the couples of the battery can act more or less as voltameters, and decompose part of the sulphate of zinc they produce. Thus there is deposited on the platinum a quantity of zinc which at first is very small, and which increases in proportion as the quantity of sulphate of zinc increases in the liquid of the battery, a quantity which always replaces an equivalent weight of hydrogen, the formation of which is no longer due to electrolysis. The zinc thus deposited in the battery itself, and from which it borrows the heat necessary for its separation, dissolves immediately in the ratio of its production, replacing the heat which has been borrowed. This action, in fact, is completely local, and does not aid the current, the enfeeblement of which is indicated by a smaller deflection of the needle, and by a retardation of the chemical action.

When the operations succeed one another without renewing the acid of the battery, the quantity of zinc in solution continually increases, and the electrolysis we have mentioned is evidenced by a smaller deflection of the needle, and by the retardation of the chemical action. A moment is attained at which the zinc is deposited in too large a quantity to dissolve immediately in sulphuric acid which is gradually weaker, and an end must then be put to the operation.

. The compound SO^3 (anhydrous sulphuric acid), when quite pure, placed in a large excess of water, disengages 18639 thermal units (XII.). This experimental datum and the following data are necessary for the discussion of the electrolysis of sulphuric acid :—

			Quantity of water, in equivalents.	Thermal units.
XIII. Solution of				
anhydrous sulphate of zinc	.	162	9553
,,	,,	copper .	160	8465
,,	,,	cadmium	208	5432
,,	,,	hydrogen	110	8821
XIV. Solution of				
crystallized sulphate of zinc .	.	144	2240
,,	,,	copper .	125	1393
,,	,,	cadmium	140	1493

I have endeavoured to account for the influence which liquids submitted to electrolysis exert upon the distribution of heat in the voltaic circuit. For this I have investigated this action, allowing for (1) their degree of concentration, (2) the distance of the plates immersed, (3) the extent of the moistened surface, (4) the nature of the liquids.

Thus, for instance, to investigate the influence of the concentration of the liquids, I worked with 100 cubic centims. of liquid containing 101·55 grms. of sulphuric acid (SO^4H) in a litre, which served as a standard of comparison, and with equal volumes of this liquid gradually more and more diluted. I reached a dilution of $\frac{1}{128}$, the liquid containing then only 0·0793 grm. of sulphuric acid in the 100 cubic centims. employed. I took care to have the experiments made with the more or less diluted acid succeeded or preceded by experiments made with the acid which served as standard of comparison.

I have varied the distances, so as to ascertain the part to be assigned to the heat produced in the work of giving a definite position to the molecules of the electrolyte in the body of the liquid.

To ascertain the influence of the nature of the liquids, I have worked as follows :—

I have retarded, as much as possible, the chemical action of the battery, by placing in the calorimeter which contains it a rheostat with great resistance; and I have successively introduced into the exterior of the circuit voltameters with plates of copper, of cadmium, and of zinc. I have taken care to precede or succeed each of these experiments by another in which the voltameter was dispensed with. In a second series of experiments I placed

the voltameters in a second calorimeter. Lastly, in a third series of experiments I suppressed the rheostat.

Replacing the solution of sulphuric acid in the voltameter with platinum plates by an equivalent solution of nitric acid, and working alternately with each solution, I found that nitric acid borrows for its decomposition about 1062 thermal units less than sulphuric acid, and that consequently the radical $N^2 O^6$, in combining with ordinary hydrogen, disengages 46462 thermal units (heat of formation of sulphuric acid) -1062; that is, 45400 thermal units.

I may be permitted, in conclusion, to offer the following considerations :—

The experiments the results of which I now detail by no means invalidate the conclusions I have considered myself justified in drawing from the results of my former experiments*.

Chemical reactions (combinations or decompositions) are complex; that is, the molecules concerned undergo modifications which precede the combination or which follow the decomposition. These modifications are manifested by a phenomenon of absorption or of disengagement of heat quite independent of the thermal phenomenon which accompanies the combination or the chemical separation.

These modifications which the molecules of bodies, as yet undecomposed, undergo, and which reveal themselves by the force they develope, explain the necessary action of heat, of light, and of electricity as determining causes of combinations—for instance, in the formation of water, hydrochloric acid, &c.

The oxyacids only differ from the hydracids in this, that the metalloid they contain is compound.

The hydracids I have investigated, and in which the metalloid is compound, appear constituted like the hydracids where the metalloid belongs to the natural family that comprehends chlorine, bromine, and iodine. They appear formed by the combination without condensation of two volumes of each of the constituent elements.

I give the heat of formation of these acids, and of some of their salts.

The constituent elements of these compounds are not in the condition we know them in the free state ; for they disengage heat on passing from the *nascent* to the *ordinary* state.

What I have said as to the condition of the constituent elements of saline compounds may also be applied to the condition of the constituent elements of water and of the metallic oxides.

Water is not an electrolyte ; for it cannot be *directly* decom-

* *Comptes Rendus des Séances de l'Académie des Sciences*, vol. xiii p. 369.

posed by even the most energetic voltaic current capable of *directly* effecting the chemical separation of compounds far more stable than it. Hence it is not the nascent hydrogen which liberates the metal of the salts held in solution in the voltameter.

Assuming that water could be decomposed by the voltaic current, the secondary phenomenon of the reduction of salts would be inadmissible—in the case of sulphate of zinc, for instance. In fact, in the voltameter, nascent hydrogen cannot be substituted for the zinc of sulphate of zinc; while in the battery it is the contrary phenomenon, of the substitution of zinc for the hydrogen of the sulphate of hydrogen, which produces the current.

Assuming also that, contrary to Faraday's law, the voltaic movement could effect the double electrolysis of water into its simple elements (acid and metallic oxide), the reduction of metallic oxide by nascent hydrogen (which as an extreme case might be conceived to extend to oxide of copper) is inadmissible in the case of oxide of zinc, and with still greater reason in that of oxide of potassium.

Water constitutes, then, the very mobile medium in which the electrolyte can freely move and adjust itself, in conformity with the explanation which Grotthüss has given of the transport to the two poles. This water can only be decomposed (in an indirect manner) by the battery in case its tension is great enough to allow the current to traverse the space separating the electrodes, and to raise the temperature sufficiently for a repetition of Grove's experiment of the decomposition of water by incandescent platinum.

It would seem that the chemical action produced in the battery, and which puts in play the constituent molecules of the saline compounds, produces in the circuit a very simple motion, which can only be transmitted to the constituent molecules of compounds of the same order. Thus the chemical decomposition of these compounds may be produced when the number of couples is so multiplied that the voltaic motion developed acquires a sufficient amplitude to transport the constituent molecules outside their sphere of activity.

Thus nitric acid, which cannot be *directly* deoxygenized in the voltaic circuit (from which it need not, however, borrow much heat), is *directly* decomposed, borrowing a much more considerable quantity of heat; but it is as a saline compound—that is, with the separation of the metalloid NO^6 and of the metal H.

I have showed[*] that a pressure of about 85 atmospheres does not oppose the decomposing action of the current.

[*] " Researches on the Influence of Pressure on some Physical and Chemical Phenomena," *Comptes Rendus de l'Académie des Sciences,* vol. li. pp. 827 & 1027.

The deflection of the needle of a tangent-compass, as well as the duration of operation, may well show the quantity of chemical action produced in each couple in equal times; but the calorimeter alone can give the quantity of heat at work in the element—a quantity which in the same time and for the same deflection of the needle increases with the number of couples. The use of several calorimeters, containing the battery and the various parts of the interpolar, enables us to measure the distribution in the circuit of the motive force developed in the battery, and to assign their respective parts to the complicated reactions.

If we admit that the tangent-compass measures the number of *electrodynamic vibrations* in the voltaic circuit, we are led to the conclusion that the calorimeter measures '*the magnitude and velocity of these vibrations.*

The compound metalloid radicals either decompose water in a manner opposite to that of the alkaline metals, combining with its hydrogen and thus reproducing the acid decomposed, or they decompose into oxygen (which is liberated) and a body (such as SO^3 for the radical SO^4) which combines with water and also reproduces the decomposed acid.

Knowing the heat of formation of dilute sulphuric acid, starting from sulphur [*] , from the compound SO^3, and the metalloid radical SO^4, it is easy to calculate the heat of formation of the two latter.

In a Smee's couple placed in the calorimeter, a considerable portion of the heat developed by the chemical action remains imprisoned in the calorimeter, and cannot be expended in the interpolar in producing useful work. This quantity of heat, represented by about 6000 thermal units, and which remains confined within the battery, is produced in the passage of hydrogen from the nascent to the ordinary state.

We may make the same remark with regard to the battery formed with Smee's elements—with this observation, that to this first quantity of heat, necessarily lost as regards useful work, a second must be added, which is accidentally lost in the couples where it is produced, and where it is used in the partial electrotrolysis of the sulphate of zinc formed there.

The quantity of heat restricted to the battery, and which is represented by about 6000 thermal units, would doubtless be higher if the nascent hydrogen, in becoming ordinary hydrogen, did not pass into the gaseous state.

This quantity of heat, which it is impossible to transfer outside the element, cannot be attributed to the solution in water

* Mechanical Researches on Compounds in Multiple Proportions (Thesis, 1853), and *Journal de Pharmacie et de Chimie*, 3rd ser. vol. xxiv. pp. 241, 311 & 412 (1853).

of anhydrous sulphate of zinc directly formed in the element; for, were this the case, the quantity of heat thus confined would be 9553 instead of 6000 thermal units. Moreover, if it be admitted that the hydratation of sulphate of zinc and its complete solution constitute a distinct phenomenon, completely independent of the phenomena directly produced in the voltaic circuit, it must be conceded that the inverse phenomenon of the dehydratation of sulphate of hydrogen (which would absorb 8821 thermal units) is equally independent; from which it would follow that the quantity of heat confined within the element would no longer be about 6000, but rather 9553−8821, or 732 thermal units.

As regards the quantity of heat which the work of the adjustment of the molecules may require, it is so small that it may be neglected.

The concentration of the liquids, their nature, the distance of the plates immersed, do not exert any considerable influence on the distribution of heat in the circuit, and therefore do not modify its resistance to any appreciable extent. The influence of the extent of surface of the plates immersed appears to be much more pronounced. Although I am not in a position to publish now all the results of my experiments, I think I may state, in conclusion, that *the phenomena produced in the couples, and the actions produced in the interpolar circuit, may be completely explained by a calculation of the* vires vivæ *destroyed and the motive force produced.*

XXXV. *Note on a Lecture-Experiment.*
By C. Hockin, *M.A.*[*]

THE little apparatus shown in figs. 1 and 2, arranged by Dr. Matthiessen and myself, was lately exhibited at the Royal Institution. The object of the apparatus is to show the identity of the conducting-power of the metals for heat and for electricity. In fig. 1 we have a number of glass bulbs with tubes attached dipping into a coloured solution, forming a series of electrical air-thermometers. In each bulb is fixed one of the wires to be compared. The ends of these wires are soldered to thick copper wires pass-
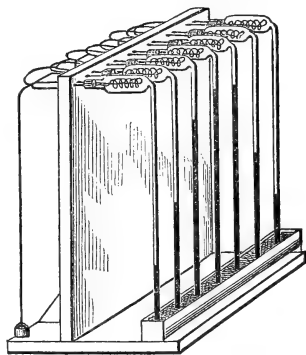
Fig. 1.
(Scale one-tenth of the natural size.)

* Communicated by the Author.

ing through the corks which stop the tubes, and then through a stout upright board so as to support the bulbs. Of the thick wires, one from each tube is soldered to one thick copper wire, and the other to another thick wire. These last wires are connected with the poles of a battery of one or two large Grove's cells.

The current then divides itself, and a portion flows through each wire proportional to the conducting-power of that wire. This current heating the wire causes the air in the bulb to expand and depress the liquid in the tube attached by an amount nearly proportional to the conducting-power of the wire. If the tubes were filled at first to the top, the liquid will, when the current is flowing, fall through different amounts. Fig. 1 shows the curve when the wires are gold, silver, and various alloys of gold and silver. If the connexions are changed so that the same current flows in succession through every wire, the liquid will be depressed by an amount nearly proportional to the resistance of each wire.

In fig. 2 we have a similar set of bulbs, into each of which

Fig. 2.

(Scale one-tenth of the natural size.)
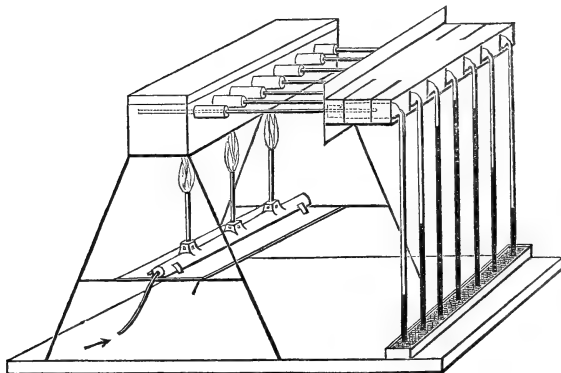
passes, through a cork, a bar of metal of the same material as the wire in the corresponding bulb, fig. 1.

The metal bars are at their other end secured in a box of boiling water. The heat conducted by the bars from the box of water to the bulb depresses the liquid in the tubes, and a curve is formed by the tops of the columns of liquid of nearly the same shape as was formed by the heated wires.

It is well to protect the bulbs in both cases by enclosing them in little compartments formed of blackened tin-plate. These may be conveniently formed by soldering pieces to form the ver-

tical walls of each compartment to a plate at the back. This plate has holes bored in it, through which the bars pass. A plate of metal at the top and bottom close in the bulbs completely ; and the plates are secured in their places by four wires bent twice at right angles and serving as clamps, as indicated in the figure.

XXXVI. *Notices respecting New Books.*

Notes on the History, Methods, and Technological importance of Descriptive Geometry, compiled with reference to Technical Education in France, Germany, and Great Britain. By ALEXANDER W. CUNNINGHAM. Edinburgh: Edmonston and Douglas. 1868. (Pp. 58.)

THE titlepage of this tract almost sufficiently describes its contents. After a brief historical sketch of the various methods of representing solids *in plano* up to the time of Monge, the author gives in general terms an account of the method of Descriptive Geometry. He points out that the most fundamental department of industrial art is that of Shaping matter by Tools, which is in fact constructive solid Geometry. To this art that of Descriptive Geometry is strictly correlative, inasmuch as it exhibits graphically on a plane what the other realizes in solid matter; in fact the working drawings commonly used in carpentry, stone-cutting, &c. are nothing but particular cases of an art which Descriptive Geometry treats generally.

In the latter part of the tract the author notices the position assigned to the study of this subject in France and Germany, in contrast with the scanty attention paid to it in England. He remarks that whatever has been done in this country has directly originated from government schools, and urges that this shows Government to have been in this matter far ahead of the people.

It is scarcely necessary to add that we thoroughly agree with Mr. Cunningham as to the value of Descriptive Geometry, both in regard to its direct applications to the arts, and to its use as an exercise for clearing the student's conceptions of geometrical combinations in space of three dimensions.

XXXVII. *Proceedings of Learned Societies.*

ROYAL SOCIETY.

[Continued from p. 241.]

February 20, 1868.—Dr. William Allen Miller, Treasurer and Vice-President, in the Chair.

THE following communication was read :—
" On the Resistance of the Air to the Motion of Elongated Projectiles having variously formed Heads." By the Rev. F. Bashforth,

B.D., Professor of Applied Mathematics to the Advanced Class of Artillery Officers, Woolwich.

These experiments were undertaken with a view to determine the resistance of the air to some forms of heads of elongated shot which were likely to be of practical use. The chronograph used was the one described in the Proceedings of the Royal Artillery Institution for August 1866*, which was constructed on the plan of the Greenwich instrument. Ten screens were placed in a line at intervals of 150 feet, the first being 75 feet from the gun. The following were the forms of the heads, and ten shot of each kind were prepared :—

(1)   Hemispherical .... solid.
(2)   Hemispheroidal (axes as 1 : 2) .... solid.
(3)   Ogival (struck with a radius = 1 diameter).. solid.
(4)   Ogival (struck with a radius = 2 diameters).. solid.
(5)   Ogival (1 diameter) .... hollow.
(6)   Ogival (2 diameters) .... hollow.

(3) and (5) as well as (4) and (6) had respectively the same external forms, but the solid were nearly double the weight of the hollow shot. The gun used was a 40-pounder M.L., and the diameter of the shot was 4·7 inches.

It was found, as in the trial experiments of 1865, that, if s be the space described in time t after passing the first screen, then, approximately,

$$t = as + bs^2,$$

from which it follows that, if v be the velocity at time t,

$$v = \frac{1}{a + 2bs},$$

and the retarding force

$$= -2bv^3.$$

If V denote the velocity when $s = 0$, then

$$V = \frac{1}{a},$$

and

$$v = \frac{1}{\dfrac{1}{V} + 2bs}.$$

All the hollow shot were fired, giving eighteen out of twenty successful shots. Only a part of the solid shot prepared were fired ; and they did not give nearly such good results as the hollow shot, probably in consequence of the superior angular velocity of the hollow shot—because, as a 5-lb. charge was used throughout, the lighter shot had a higher initial velocity, and consequently a higher corresponding angular velocity.

Tables are given showing for every round :—(1) the experimental determination of the time of passing each screen, supposing the first screen to be passed when $t = 0$; (2) the velocities at the middle points between successive screens ; (3) the weights of the shot ; and

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* Published separately by Bell and Daldy, 1866.

(4) the numerical values of bl^2, where $l=150$ feet, the distance between the screens. And *assuming* that, for a given form of head, the resistance of the air varies as the square of the diameter, the mean values of $2b$ have been adopted for shot weighing W lbs., and having a diameter of d inches, or 2R feet.

When a body is moving in a straight line under the action of a force which varies as the cube of the velocity, it appears that the actual velocity v' at the middle of any space $2s'$ is such that, if another body moved over the same space $2s'$ with a *uniform* velocity v', it would describe it in the same time as the first-named body. For the time t' would

$$= \frac{1}{V} 2s' + b(2s')^2,$$

uniform velocity

$$= \frac{2s'}{t'} = \frac{2s'}{\frac{1}{V} 2s' + b(2s')^2} = \frac{1}{\frac{1}{V} + 2bs'} = v',$$

the actual velocity at the distance s'.

M. Hélie, in his 'Traité de Balistique' (1865), adopted, for elongated projectiles, a law for the resistance of the air which varied as the velocity cubed. The law was deduced from some experiments made at Gâvre, when a great number of velocities (v', v'') of shot fired with various charges were measured at two points x metres apart. The mean values of v' and v'' were taken and substituted in the formula $\frac{v''-v'}{v''v'x}$; and it was found that this was approximately constant, and consequently that the resistance varied as the (velocity)[3]. The French measures and weights have been converted into English measures for M. Hélie's best experiment, in order to facilitate comparisons with my own experiments. The contents of M. Hélie's work were quite unknown to me for several months after my report on the above experiments had been given in. For an ogival-headed shot struck with a radius of two diameters M. Hélie's value of $2b$ is

$$2b = \cdot000036 \frac{R^2}{W} = \cdot000000062 \frac{d^2}{W},$$

while my experiments for the same form of head, but with much higher velocities, give

$$2b = \cdot000060 \frac{R^2}{W} = \cdot000000104 \frac{d^2}{W}.$$

There is reason to expect that my value of b will require a small reduction for the low velocities used in M. Hélie's experiments; but it is extremely improbable that it can be reduced to M. Hélie's value. It will thus appear that M. Hélie and I agree in adopting a law of the resistance of the air, but that we have followed quite independent methods in experimenting, and have arrived at different numerical results.

Feb. 27.—Lieut.-General Sabine, President, in the Chair.

The following communication was read :—

" On the Resistance of the Air to Rifled Projectiles." By J. A. Longridge, C.E.

The introduction of elongated rifled projectiles having rendered it necessary to reconsider the laws of resistance which had been deduced by Robins, Hutton, and more recent authors, such an investigation is the object of this paper.

It is first shown that Hutton's law,

$$R = av + bv^2,$$

if applied to the results obtained by the Special Armstrong and Whitworth Committee, 1866, leads to the following equation,

$$x = 1620 \log_{10} \left\{ \frac{V - 1015 \cdot 4}{v - 1015 \cdot 4} \right\},$$

where V is the initial velocity,

v the residual velocity at the distance x from the gun.

In like manner it is shown that the law adopted by Piobert,

$$R = Av^2 + Bv^3,$$

leads to the equation

$$x = 2197 \log_{10} \left\{ \frac{V - 994}{v - 994} \cdot \frac{v}{V} \right\},$$

and the law

$$R = Av^3 + Bv^4$$

to the equation

$$x = 2668 \log_{10} \left\{ \frac{V^2 - 958850}{v^2 - 958850} \cdot \frac{v^2}{V^2} \right\}.$$

These equations all fail by x becoming infinite when $v = 1015$, 994, and 979 respectively.

It is, however, observed that, in the assumption of the law of the resistance, the higher the power of velocity the longer does the corresponding equation give rational results ; and by assuming $R = av^p$ with the same data, the following equation was obtained,

$$x = \frac{\log^{-1} 23 \cdot 618}{V^{8 \cdot 747}} \left\{ \left(\frac{V}{v} \right)^{8 \cdot 747} - 1 \right\},$$

which gives consistent results for all values of v.

The value of p here is $8 \cdot 747$, which would give the resistance varying nearly as the ninth power of the velocity.

This result led the author of the paper to doubt the accuracy of the experiments, and to seek for further and more correct data, which were obtained from a minute (No. 23,351) of the Ordnance Select Committee, dated 21st September 1867, containing the results of experiments showing the loss of velocity of two projectiles, one of 8·818 lbs., and the other of 251 lbs., in passing through certain given distances with given initial velocities, varying from about 1500 feet to 600 feet per second.

From these results a diagram was constructed, and for each pro-

jectile an equation was found which agreed tolerably well with the experimental results.

The form of the equation assumed was

$$(x+a) v^n = C \; ;$$

and the resulting equation was for the small shot

$$(x+665) v^{2\cdot4} = \log^{-1} 10\cdot1473853,$$

and for the large shot

$$(x+2032) v^3 = \log^{-1} 12\cdot6696158,$$

the maximum error being about $1\frac{1}{2}$ per cent. of the velocity.

Introducing into these equations the diameter and weight of the respective projectiles, and taking the index $n=2\cdot5$, the values of C were found to be,

$$\text{small shot,} \qquad C=\log^{-1} 10\cdot7295585 \; \frac{W}{d^2},$$

$$\text{large shot,} \qquad C=\log^{-1} 10\cdot7454405 \; \frac{W}{d^2},$$

$$\text{the mean being } C=\log^{-1} 10\cdot7375745 \; \frac{W}{d^2},$$

and the resulting general equation

$$\left(x+\frac{\log^{-1} 10\cdot7375745 \,.\, W}{d^2\, V^{2\cdot5}}\right) \frac{d^2 \,.\, v^{2\cdot5}}{W} = \log^{-1} 10\cdot7375745.$$

The maximum error in velocity, as calculated by this formula, was for the small shot $1\frac{1}{2}$ per cent., and for the large shot $2\frac{1}{2}$ per cent.

From the above equation the resistance per square inch of sectional area is found,

$$R = \frac{v^{4\cdot5}}{\log^{-1} 13\cdot0154756},$$

from which the following Table is constructed, the third column showing the resistance, as calculated by Hutton's formula :—

Table of Resistances to a Rifled Projectile.

Velocity, feet per second.	Resistance, in lbs., per square inch.	Hutton, p. 218.	Velocity, feet per second.	..stance, in per square inch.	Hutton, p. 218.
1500	18·89	18·94	700	0·613	3·12
1400	13·87	16·23	600	0·306	2·20
1300	9·94	13·67	500	0·135	1·49
1200	6·92	11·29	400	0·0494	0·93
1100	3·722	9·14	300	0·01354	0·52
1000	3·052	7·24	200	0·00218	0·23
900	1·900	5·61	100	0·0000965	0·556
800	1·118	4·24			

It is next shown that the hypothesis of the great increase of resistance at velocities exceeding 1100 feet per second being due to the vacuum behind the projectile is untenable, because the actual

resistance at 1300 feet per second is only 9·94 lbs. per square inch, whilst, according to that hypothesis, the back resistance alone would be 15 lbs. per square inch.

It is suggested that the true reason of the great increase of resistance may be found in the fact that a wave-impulse cannot be propagated at a greater velocity than 1100 feet per second, and that consequently a great condensation of air must take place in front of the projectile at all velocities exceeding this, and the resisting force of such condensed air will increase at a greater rate than indicated by Mariotte's law, owing to the evolution of heat due to the condensation.

A comparison is then instituted between the resistances as ascertained by the above law and those given by Hutton's formula.

It is stated that in experiments made on May 17th, 1867, the small shot weighing 8·8 lbs., moving with a mean velocity of 986 feet per second, lost $58\frac{1}{2}$ feet of velocity in a distance of 900 feet.

The time of flight being ·96 of a second, the resisting force must have been nearly twice the weight of the shot, or more accurately 17·2 lbs.

Now, according to the formula given in this paper, the resistance is found to be 17·75 lbs., whilst Hutton's formula gives a resistance of $46\frac{1}{2}$ lbs.

Having thus obtained a law which gives, with considerable accuracy, the residual velocity at any point of the flight, the corresponding equation to the trajectory is deduced for low degrees of elevation when the length of the arc differs very slightly from the horizontal distance, or $ds = dx$ nearly; and the following is the resulting equation:—

$$y = x \tan\phi + A \left\{ \frac{n}{2(n+1)} a^{\frac{2(n+1)}{n}} + a^{\frac{n+2}{n}} x - \frac{n}{2(n+1)} (x+a)^{\frac{2(n+1)}{n}} \right\},$$

where $A = \dfrac{g}{2} \cdot \dfrac{n}{n+2}$, and c and a are the constants, and n the index

$C^{\frac{2}{n}}$

in the general equation $\qquad (x+a)\, v^n = C.$

Examples of the application of this are given, showing the calculated elevation for the 12-pounder muzzle-loading Armstrong gun for ranges of 2855 yards and 4719 yards, the gun being 17 feet above the planes.

The calculated elevations were 6° 56′ and 14° 6′, the actual elevations being 7° and 15° respectively.

It is not intended to claim more than approximate accuracy for the formulæ in this paper. The general formula has been shown to be derived by taking mean values of n and c, whereas the actual results would indicate that the value of n increases with the diameter of the projectile; and it is shown in a note that the values of n which agree best with experiment are,

for the small shot $n = 2·4$,
for the large shot $n = 4$,

corresponding to the following resistances,
<div style="text-align:center">small shot $R=v^{4\cdot4}$,</div>
<div style="text-align:center">large shot $R=v^6$.</div>

Whether in reality the index does increase with the diameter of the shot must be left to be determined by more extended experiments; meantime it may be assumed that the general formula in this paper represents with tolerable accuracy the law of resistance and the loss of velocity of projectiles varying from 8·8 lbs. to 251 lbs. in weight, from 3 inches to 9 inches in diameter, and from 1500 to 600 feet per second in velocity.

ROYAL INSTITUTION OF GREAT BRITAIN.

February 14, 1868.—" On Vanadium, one of the Trivalent Group of Elements." By Henry E. Roscoe, B.A., F.R.S.

The metal vanadium (so called from Vanadis, a cognomen of the Scandinavian goddess Freia) was discovered in 1830 by Sefström in the celebrated Swedish bar-iron made from the Taberg ore. From this source, even when using many pounds of the iron, Sefström obtained only minute quantities of the new substance; but he found it in somewhat larger amount in the slag or cinder produced in the reduction of the iron ore. Sefström ascertained some of the most peculiar characters of the substance, proved it to be a new element, and prepared some of its compounds in the pure state. The reactions by which vanadium can be separated and distinguished from all the other elements are :—(1) The formation of a soluble sodium vanadate when the vanadium compounds are fused with sodium carbonate ; (2) the formation of an insoluble ammonium vanadate when sal-ammoniac is added to the solution of a soluble vanadate ; (3) the production of a splendid blue solution when this ammonium-salt, dissolved in hydrochloric acid, is warmed with reducing agents such as oxalic acid.

Sefström, not having leisure to prosecute the full examination of the properties of the new metal, handed over his preparations to Berzelius; and it is to the investigations of the great Swede (1831) that we owe almost all our acquaintance with the chemistry of vanadium.

Since Berzelius's time vanadium has been discovered in many minerals, of which a lead ore containing lead vanadate and called by the mineralogists vanadinite, is the most important. It has also been found in many iron ores, in clay, bricks, and even in caustic soda. Still the quantity of the substance found in all these various sources has been extremely small—so much so, that the vanadium compounds must be reckoned amongst the greatest of chemical rarities, and we find them quoted in the price-lists of dealers in chemicals at 1s. 6d. per grain, or £35 per ounce ! It is clear that our knowledge of the chemical properties of a substance so rare must necessarily be but incomplete, as the difficulties of obtaining exact or satisfactory results with small quantities of material are evident ; and, in fact, the statements of the only persons who have worked upon the subject recently (Schafarik, Czudnowicz), instead of giving us any more

reliable information respecting the character of vanadium, have only served to throw doubt upon some of the conclusions of Berzelius, and thus to show that our knowledge is even less complete than it appeared to be.

Hence it was with much satisfaction that in February 1865 the speaker came into possession of a plentiful source of vanadium in a by-product obtained in the preparation of cobalt from the copper-bearing beds of the lower Keuper Sandstone of the Trias at Alderley Edge, in Cheshire. The manager of the works was puzzled to know why a blue solution, supposed by him to contain copper, did not deposit the red metal upon a strip of zinc ; the speaker recognized this reaction as due to the presence of vanadium, and secured the whole of the by-product, which he found to contain about 2 per cent. of the rare metal. The exact position of the vanadium mineral in the sandstone beds cannot now be stated, as the mine (at Mottram, St. Andrews) from which the cobalt ore was obtained is now closed and cannot be entered. The general characters of the deposit, however, are well known, and exhibit points of great interest ; they have been well described by Mr. Hull as follows :—

" The ' edge ' or escarpment of Alderley rises from the eastern side of the plain of Cheshire gradually towards the east, but with a steep and abrupt ridge towards the north. This northern bank is richly wooded, and has a very beautiful aspect when viewed from a distance, as it contrasts strongly with the almost level plain which sweeps away to the northward and westward from its base. The ridge has here been upheaved along the line of a large fault, bearing east and west, throwing down at its base the red marl, and on the other side bringing up the soft sandstone of the Bunter, capped by a mural cliff of lower Keuper conglomerate, which often breaks out in conspicuous masses through the foliage. The beds rise from the plain towards the east at an angle of about from 5° to 10° ; and the escarpment is continued southward for some distance facing the east."

Succession of Beds in Descending Order (Hull).

Red marl........................		{ Red and gray laminated marls.
Waterstones .... Freestone .... Copper-bearing sandstone Conglomerate......... }	Lower Keuper sandstone, 500 feet.	Brownish flaggy sandstones and marls. White and brown freestone. Soft white, yellow, and variegated sandstone. Hard quartzose conglomerate, underlain by bands of marl, forming the base of the Keuper sandstone.
Upper red and mottled sandstone .... }	Bunter.	Soft fine-grained yellow and red sandstone, being the uppermost member of the Bunter sandstone.

The beds in the above series which claim the greatest share of our attention are those at the base of the Keuper series, for in these occur the copper and other minerals. The copper, as both blue and green carbonate, occurs disseminated throughout the sand, the ore coating the outside of the grains of sand and the pebbles of quartz. In addition to copper, bands containing lead, both as carbonate and sulphide (galena), occur, also bands and veins of cobalt-ochre, oxide of manganese, and iron-ochre in workable quantity. The copper is extracted from the ore by solution in hydrochloric acid and precipitation as metal by scrap iron. The ordinary copper liquor, as well as the oxide of iron precipitated by lime from the solution of the chloride, does not contain any trace of vanadium ; nor was the speaker able to detect any of this metal in the ore as at present worked.

Following, in the main, the process of preparation adopted by Sefström, the speaker obtained from the above-mentioned lime precipitate several pounds of pure ammonium vanadate, from which all the other compounds of vanadium can be prepared.

What now were the conclusions to which Berzelius arrived from his experiments concerning the constitution of the vanadium compounds? He corroborated Sefström's statement, that the most characteristic feature of the substance is the existence of an acid-forming oxide, termed vanadic acid, produced whenever any of the oxides are heated in the air. Berzelius also discovered two other oxides of vanadium (of which he ascertained the composition), and likewise a volatile chloride. To the highest oxide he gave the formula VO^3, to the second VO^2, and to the lowest (or suboxide) VO ; whilst the chloride was represented by VCl^3. The atomic weight of the metal he ascertained to be $V = 68\cdot5$. Berzelius came to this conclusion from the following experimentally ascertained facts : (1) that on passing hydrogen over heated vanadic acid a constant loss of weight occurred, and the suboxide was formed ; (2) that when dry chlorine was passed over the suboxide thus prepared, the volatile chloride was formed, and a residue of vanadic acid remained which was exactly equal in weight to one-third of the acid originally taken for reduction. Hence, assuming that the lowest oxide contains one atom of oxygen (an assumption borne out by the analysis of the chloride), the acid must contain three atoms of oxygen[*]; and the following formulæ represent the composition of these compounds according to Berzelius :—

$$VO, \qquad VO^2, \qquad VO^3, \qquad VCl^3. \qquad (V = 68\cdot5.)$$

The interest attaching to the conclusions which Berzelius fairly drew from his experiments was much heightened by an observation made by Rammelsberg in 1856, as to the exact crystalline form of the mineral vanadinite, a double salt of lead vanadate and lead chloride.

So long ago as 1780, Werner had observed the identity of crystal-

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[*] Berzelius concludes that the acid does not contain two atoms of metal, inasmuch as no alum could be formed with potassium sulphate corresponding to those formed by well-known sesquioxides.

line form of two minerals, viz. apatite (a phosphato-fluoride of calcium), and pyromorphite (a phosphato-chloride of lead), to which may be added mimetesite (an arsenato-chloride of lead).   These minerals all have an analogous composition, being represented by the formulæ

$$Apatite \ldots\ldots\ 3(Ca^3\,P^2\ O^8) + CaFl^2$$
$$Pyromorphite \ldots\ 3(Pb^3\,P^2\ O^8) + Pb\,Cl^2$$
$$* \ Mimetesite \ldots\ 3(Pb^3\,As^2\,O^8) + Pb\,Cl^2.$$
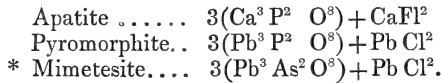
They are truly isomorphous, crystallizing in hexagonal prisms, terminated with hexagonal pyramids, having the same angles and the same length of axes.   Rammelsberg added to this list the mineral vanadinite, which he ascertained by measurement to be strictly isomorphous with the foregoing, and to be as follows:—The angle P on P was in

(1) Vanadinite .. $142\overset{\circ}{\ }\ 30\overset{'}{\ }$ | (3) Pyromorphite . $142\overset{\circ}{\ }\ 15\overset{'}{\ }$
(2) Apatite .... $142\ \ 20$ | (4) Mimetesite .. $142\ \ \ 7$

and the relation of the length of the axis,

(1) $1 : 0\cdot727$ | (3) $1 : 0\cdot736$
(2) $1 : 0\cdot732$ | (4) $1 : 0\cdot739$

So far, indeed, has the identity of crystalline form been traced, that crystals have been found which at one end consisted of vanadinite, and at the other of pyromorphite (Heddle). Now, judging from the crystallographic analogies alone, we shall conclude that the formula of vanadinite is

$$3(Pb^3\,V^2\,O^8) + Pb\,Cl^2 \dagger,$$
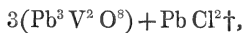
the oxide of vanadium contained in the mineral having a formula $V^2\,O^5$, agreeing with the corresponding oxides of phosphorus and arsenic, $P^2\,O^5$ and $As^2\,O^5$. In making this assumption, however, we are at once confronted with the unyielding chemical facts of Berzelius, according to which the oxide in question must be represented by the formula $V\,O^3$, and contains three, and not five, atoms of oxygen.

It is evident, then, that we have here either to do with an exception to the law of isomorphism, or else Berzelius's views are erroneous.   Until this latter has been proved to be the case, however,

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* This group of minerals may be considered as calcium triphosphofluorhydrine, &c., thus :

$$\left.\begin{array}{l}3(PO''')\\Ca^5\end{array}\right\}\ O^9 \qquad \left.\begin{array}{l}3\,PO'''\\Ca^5\end{array}\right\}\ O^9$$
$$Fl \qquad\qquad\qquad Cl$$
$$Apatite. \qquad\ \ Pyromorphite. \qquad (Würtz.)$$
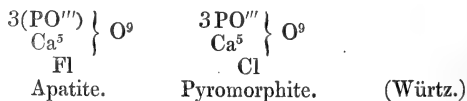
† Or lead trivanadochlorhydrine,

$$\left.\begin{array}{l}3\,VO'''\\Pb^5\end{array}\right\}\ O^9$$
$$Cl$$
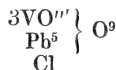
chemists have only been justified in assuming the former alternative to be the correct explanation.

The speaker stated that, in order to endeavour to clear up this question, he had most carefully repeated Berzelius's experiments, and that he had confirmed them in every particular; but having pursued the subject further than Berzelius, he had at last come to conclusions concerning the constitution of the vanadium compounds totally different from those drawn by the Swedish chemist, and had succeeded in obtaining the key to the enigma presented by the above anomalous crystallographic relations.

The speaker has proved that the substance supposed by Berzelius to be vanadium, $V = 68{\cdot}5$, is not the metal, but an oxide, and that the true atomic weight of the metal is $68{\cdot}5 - 16 = 52{\cdot}5$ (or rather, according to the speaker's exact determinations of the atomic weight, $67{\cdot}3 - 16 = 51{\cdot}3$)*. The highest oxide, the vanadic acid, $V O^3$, of Berzelius, hence becomes a pentoxide, $V^2 O^5$, corresponding to $P^2 O^5$ and $As^2 O^5$, and the isomorphism of vanadinite with the pyromorphite group of minerals is fully explained. The suboxide of Berzelius is a trioxide, $V^2 O^3$, whilst the terchloride ($V Cl^3$) of Berzelius is an oxychloride, having the formula $V O Cl^3$, and corresponding to oxychloride of phosphorus, $P O Cl^3$. The oxide supposed by Berzelius to be the metal contains $51{\cdot}3$ parts by weight of vanadium to 16 parts by weight of oxygen; and the vanadic oxide of Berzelius also exists, containing $51{\cdot}3$ parts of the metal to 32 parts of oxygen; to these oxides the empirical formulæ $V^2 O^2$ and $V^2 O^4$ may be given. Thus we have the following as representing the true composition of these vanadium compounds :—

	Dioxide.	Trioxide.	Tetroxide.	Pentoxide.	Oxytrichloride.
$V = 51{\cdot}3$	$V^2 O^2$	$V^2 O^3$	$V^2 O^4$	$V^2 O^5$	$V O Cl^3$

Each of the four oxides can be obtained in the anhydrous state; the dioxide is prepared as a grey metallic powder by passing the vapour of the oxytrichloride mixed with hydrogen over red-hot carbon. The trioxide is obtained by the reduction of vanadic acid in a current of hydrogen; and the tetroxide is formed by the slow oxidation of the trioxide.

The lowest, or dioxide of vanadium ($V^2 O^2$), is obtained in solution by the reducing action of nascent hydrogen evolved from zinc, cadmium, or sodium-amalgam upon the sulphuric acid solution of vanadic acid, which, passing through all stages of blue and green

* In his paper on Vanadium, read before the Royal Society (Dec. 19, 1867), the author ventured to predict that the difference between the number he obtained ($67{\cdot}3$) and that found by Berzelius ($68{\cdot}5$) was probably owing to the fact that the vanadium compounds employed by Berzelius contained traces of phosphorus, which render the perfect reduction of the vanadic acid in hydrogen impossible. Most fortunately this supposition has been singularly verified, inasmuch as Dr. Frankland has kindly placed in the speaker's hands a small specimen of vanadate of ammonia found in Faraday's collection, and labelled " Sent to me by Berzelius, 1831." On examination, this sample was found to contain considerable quantities of phosphorus, thus confirming the speaker's previously expressed opinion.

colour, ultimately assumes a permanent lavender tint.   This solution of V^2O^2 in sulphuric acid acts as a most powerful reducing agent, bleaching indigo solution and other vegetable colouring-matters as rapidly as chlorine ; it also absorbs oxygen with avidity from the air, forming a deep-brown solution.   The other oxides of vanadium may be obtained in solution by the action of various reducing agents on the sulphuric solution of vanadic acid.   Thus, by the action of nascent hydrogen evolved from magnesium a permanent *green* tint is obtained, and the vanadium is contained in solution as the trioxide, V^2O^3 ; whilst if moderate reducing agents, such as sulphurous acid, sulphuretted hydrogen, or oxalic acid are employed, the colour of the liquid does not pass beyond the *blue* stage, and the vanadium is contained in solution as tetroxide, V^2O^4*.   The different colours of solutions containing these oxides was exhibited by means of the magnesium light.

The fact that the lemon-coloured chloride (the terchloride of Berzelius) contains oxygen was clearly demonstrated during the discourse by passing the vapour from a few grammes of the substance, together with perfectly pure hydrogen gas, over red-hot carbon.   A portion of the oxygen of the oxychloride unites with the carbon to form carbonic acid, and the presence of this gas was shown by the precipitation of barium carbonate in clear baryta-water contained in two test-tubes placed one before the other.   At the commencement of the experiment the carbonic acid was entirely absorbed by the small quantity of baryta-water contained in the first test-tube; but after some time the hydrochloric acid gas simultaneously produced by the decomposition of the chloride saturated this liquid, expelling the carbonic acid gas, which, being carried forward into the second test-tube, threw down a bulky precipitate of barium carbonate, thus showing that the turbidity could not possibly be due to the presence of any vanadium compound.   It was found quite unnecessary to place a tube containing heated copper oxide after the red-hot carbon for the purpose of oxidizing any carbonic oxide gas which might be formed, inasmuch as carbonic acid was always left in sufficient quantity to give a considerable precipitate.   No method has been found for separating the whole of the oxygen from the oxychloride ; and hence it has been impossible to make the above experiment quantitatively. Solid oxychlorides are obtained by the action of hydrogen upon the oxytrichloride, one of which resembles mosaic gold, possessing a bright metallic bronze-like lustre, and having been taken for the metal by Schafarik.

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* In his communication to the Royal Society (Bakerian Lecture, Proceedings of the Royal Society, vol. xvi. p. 220), the author gave the empirical formula VO and VO^2 to the first and third oxides of vanadium, as the molecular weights of these oxides have not been determined, and it is uncertain whether they obey the law of even atomicities, or, like the only corresponding compounds, the nitrogen oxides, are exceptions to this law.

On consideration, the author has, however, thought it best to adopt the double formula, as urged by Sir Benjamin Brodie on the occasion above referred to.

The atomic weight of vanadium was determined (1) by reducing the pentoxide to trioxide in a current of hydrogen, (2) by the analysis of the oxytrichloride. The atomic weight obtained as the mean of a large number of well-agreeing experiments is 51·3.

The metal itself has not yet been obtained; but a compound of vanadium and nitrogen has been prepared, shown by direct analysis to contain 14 parts by weight of nitrogen to 51·3 parts by weight of vanadium, corresponding to the formula VN. The existence of this compound is proof positive of the true atomic weight of the metal; and the nitride serves as the point of departure from which to seek for the metal and the true chlorides of vanadium, one of which, VCl^3, has already been prepared by the action of chlorine upon the nitride. It is a dark-brown liquid, which decomposes when thrown into water, forming a green solution containing $V^2 O^3$. The speaker demonstrated the fact that the oxychloride, $V O Cl^3$, when thrown into water decomposes with formation of a *yellow* solution of vanadium pentoxide, $V^2 O^5$; whilst the trichloride, $V Cl^3$, on being similarly treated, yields a *green* solution containing the metal in solution as trioxide, $V^2 O^3$. He then compared these reactions with the decomposition of the corresponding phosphorus compounds, $P O Cl^3$ and $P Cl^3$, forming $P^2 O^5$ and $P^2 O^3$, and rendered these reactions visible by obtaining a precipitate of yellow silver phosphate in the first case, and of black metallic silver in the second.

The characters of the vanadates themseves bear out the analogy of the highest oxide with the corresponding oxides of phosphorus and arsenic. In the first place, all the naturally occurring vanadates are tribasic; secondly, the true character of vanadic acid is shown to be tribasic by the fact that, when the pentoxide is fused with sodium carbonate, three atoms of CO^2 are liberated, and the normal or ortho-vanadate, $Na^3 V^2 O^8$ (corresponding to $Na^3 P^2 O^8$), is formed; thirdly, the so-called monovanadates are monobasic salts, corresponding to the monobasic phosphates, and may be termed metavanadates, thus, $Na VO^3$ and $Ba 2 VO^3$, whilst the so-called bivanadates are anhydrosalts.

All the reactions by which Berzelius explained the facts he discovered can equally well be represented according to the new atomic weight and constitution, thus:—

Berzelius's Formulæ.

$$V = 68·5. \quad O = 8.$$

$$(1) \quad V O^3 + H^2 = V O + H^2 O^2.$$

$$(2) \quad 3(VO) + Cl^6 = V O^3 + 2(V Cl^3).$$

New Formulæ.

$$V = 51·3. \quad O = 16.$$

$$V^2 O^5 + 2 H^2 = V^2 O^3 + 2(H^2 O),$$

$$3(V^2 O^3) + 6 Cl^2 = V^2 O^3 + 4(V O Cl^3).$$

The speaker stated that the foregoing facts clearly pointed out that vanadium, hitherto standing in no definite relation to other elements, must be regarded as a member of the well-known Trivalent or Triad class of elementary substances, comprising nitrogen, phosphorus, boron, arsenic, antimony, and bismuth.

It is true that we are still but imperfectly acquainted with many of the characters of vanadium ; but the more its nature is studied, the more points of family resemblance will be discovered, and the more close will the ties be found which bind it to the great Triad family.

The following tabular statement of the compounds of the most important members of this group clearly shows their common relations :—

Trivalent Group of Elements.

	Nitrogen.	Phosphorus.	Vanadium.	Arsenic.	Antimony.
	$N=14$	$P=31$	$V=51\cdot3$	$As=75$	$Sb=122$
Trihydrides	$N\,H^3$	$P\,H^3$	—	$As\,H^3$	$Sb\,H^3$
Trichlorides......	$N\,Cl^3$ (?)	$P\,Cl^3$	$V\,Cl^3$	$As\,Cl^3$	$Sb\,Cl^3$
Pentachlorides ...	—	$P\,Cl^5$	—	—	$Sb\,Cl^5$
Oxychlorides ...	—	$P\,O\,Cl^3$	$V\,O\,Cl^3$	—	—
Monoxides	$N^2\,O$	—	—	—	—
Dioxides	$N^2\,O^2$	—	$V^2\,O^2$	—	—
Trioxides	$N^2\,O^3$	$P^2\,O^3$	$V^2\,O^3$	$As^2\,O^3$	$Sb^2\,O^3$
Tetroxides	$N^2\,O^4$	—	$V^2\,O^4$	—	$Sb^2\,O^4$
Pentoxides	$N^2\,O^5$	$P^2\,O^5$	$V^2\,O^5$	$As^2\,O^5$	$Sb^2\,O^5$

In conclusion, the speaker remarked that vanadium was the fourth substance, supposed by its discoverer to be a metal, which had in recent years been shown to be a compound body.

Titanium.	*Uranium.*	*Niobium.*	*Vanadium.*
Wollaston, 1823.	Klaproth, 1789.	{ Hatchett, 1801.	{ Sefström and
Wöhler, 1849.	Péligot, 1849.	{ Rose, 1842–64.	{ Berzelius, 1831.
		Marignac, 1865.	

GEOLOGICAL SOCIETY.

January 22nd, 1868.—Warington W. Smyth, M.A., F.R.S., President, in the Chair.

The following communications were read :—

1. " On the Speeton Clay." By John W. Judd, Esq., F.G.S.

In tracing the history of discovery in connexion with this formation, the following epochs were pointed out by the author :—(1) the separation of the Cretaceous from the Kimmeridge beds by Prof. Phillips (1829) ; (2) the reference of the former to the Neocomian formation by MM. Agassiz, Godwin-Austen, Römer, and others (1838 &c.) ; and (3) the recognition of Portlandian beds in the series by Mr. Leckenby (1864).

Mr. Judd then proceeded to give a description of the *unique* cliff-section exposed at Speeton, which is unfortunately greatly complicated by faults and contortions, and much obscured by drift, landslips, and mining workings.

After adducing evidence, both stratigraphical and palæontological, to prove that no portion of the Speeton clay is of Gault age, the author showed that this great series of clays (probably over 1000 feet thick) belongs to no less than seven formations, viz. Upper, Middle, and Lower Neocomian, Portlandian, and Upper, Middle, and Lower Kimmeridge. These formations, as displayed in Filey Bay, were described in detail; lists of the fossils from each (drawn up with the assistance of Mr. Etheridge) were given, and their equivalents, both in this country and on the continent, pointed out; and the author concluded his paper with appendices on the fossils and the economic products of the Speeton clay.

2. " Notice of the Hessle Drift as it appeared in Sections more than forty years since." By Professor John Phillips, D.C.L., F.R.S., F.G.S.

Referring first to the difficulties formerly experienced in attempting to explain the origin of the Boulder-clays and Northern drifts more than forty years ago, without the aid of glaciers and icebergs, the author expressed his belief that the lowest gravels, resting on the chalk at Hessle, are of Præglacial date. He stated his opinion that there is no evidence of the beds in question being marine; while the abundance of mammalian remains offers a strong presumption against this interpretation. Beds of this order, composed of chalk and flint fragments, not only are unknown to occur in the midst of the Boulder-clay, but can hardly be imagined to exist there. Further, the Boulder-clay rests on them without conformity. Professor Phillips also observed that if the Hessle clay be the upper part of the great Holderness deposit, and not met with beyond the outcrop of the chalk, it must be designated a third Boulder-clay; and he concluded his paper by a detailed description of his original observations of the Hessle cliff more than forty years ago.

February 5th, 1868.—Warington W. Smyth, Esq., M.A., F.R.S., President, in the Chair.

The following communication was read:—

1. " On the Geological Structure of Argyllshire." By His Grace the Duke of Argyll, K.T., D.C.L., F.R.S., F.G.S., &c.

The object of the paper was to set forth some of the author's reasons for not accepting the views propounded by Mr. Geikie in his ' Scenery of Scotland viewed in connexion with Physical Geology.' His Grace believes that, although the atmospheric agencies of waste have produced great modifications of the surface, the form of the hills and valleys has in the main been determined by the action of subterranean forces.

In illustration of his opposition to Mr. Geikie's theory, he described a supposed case of the formation of a valley by atmospheric agencies, observing that, if the crumplings of the strata have not affected the present surface, a subsequent submergence and a fresh unconformable deposition filling in all the inequalities must have ensued, and that these new deposits must have been again raised

along different lines of elevation. Taking this new deposit to be the Old Red Sandstone, the author asks how it was removed, and points out difficulties in the way of supposing the removal to have been either by submergence or by subaërial agencies.

His Grace then stated that Mr. Geikie admits that the agencies of erosion have been guided in their work by the prevailing strike of the strata, which strike is followed along the same line by the larger faults, and by the anticlinal and synclinal axes,—at least as regards the general trend. He then pointed out that in reality all the great physical features of Scotland take the same N.E. and S.W. direction. He therefore considered that Mr. Geikie had understated the case of the coincidence of certain physical features, and had entirely omitted all mention of others, such as the appearances of subsidence and dislocation to be observed in the Western Islands, and the relations existing between dislocated sedimentary strata and apparently intrusive rocks.

In supporting his argument by special facts the Duke of Argyll endeavoured to show that the whole valley-system of Argyllshire may be accounted for either by faults, foldings, subsidences, or anticlinals, mentioning in particular that Loch Tyne occupies the bed of an enormous fault, that Loch Awe lies along the line of a great subsidence of the metamorphic slates, and that the gorge of the Brander Pass lies along the line of a great fracture connected with the subterranean movements which brought up the granites of Ben Cruachan, with many other instances of a like nature, in discussing which he especially demurred to Mr. Geikie's theory that the transverse valleys and gorges have been formed by two streams, each working backwards towards its own source, until the ridge which divided them was finally destroyed.

His Grace also remarked that the mineral condition of the granites at the time of the subterranean movements was such as would facilitate the transmission of earthquake-waves, and the condition of the slates was such as necessitated fracture when those waves were propagated beneath them.

In conclusion the author contested Mr. Geikie's statement of the symmetry of river-valleys and uniformity of mountain-heights, and contrasted the philosophy of the older geologists with that of the advocates of subaërial denudation.

February 26th, 1868.—Prof. T. H. Huxley, LL.D., F.R.S.,
President, in the Chair.

The following communications were read :—

1. " Notes on the formation of the Parallel Roads of Glen Roy." By C. Babbage, Esq., F.R.S.

Accepting the theory that these roads were formed on the margin of a lake, the author discussed the mode in which this formation took place, objecting to the view of its having occurred through the piling up of pebbles by wave-action, or the accumulation of blocks by rain washing them down the hill-side.

Mr. Babbage expressed his opinion that the material of which

the roads are formed was brought down by snow and ice slowly descending the hills until arrested on the margin of the frozen lake. On the melting of the snow and ice, it was tranquilly deposited without any further descent, and thus lay in a horizontal line.

In conclusion the author adverted to the theory of the change of isothermal surfaces within the earth, an account of which he had published in the Society's 'Proceedings' for 1834, as affording the necessary explanation of the causes which had produced the changes of climate in the district of the Parallel Roads.

2. " On the origin of smoothed, rounded, and hollowed surfaces of Limestone and Granite." By D. Mackintosh, Esq., F.G.S.

The author argued that smoothed surfaces are produced by the action of water charged with sediment and stones, and that " hollowed surfaces " are the result of coast-ice containing stones following the course of the advancing and retreating tide.

3. " On a striking instance of apparent oblique lamination in Granite." By D. Mackintosh, Esq., F.G.S.

Lines of stratification and lamination were stated by the author to be discernible in the granite rocks of Hountor, of the Kestor group, and of the Blackstone rock ; and he added that they support the idea of the aqueous origin of granite.

4. " On the Encroachment of the Sea in the Bristol Channel." By D. Mackintosh, Esq., F.G.S.

Mr. Mackintosh has obtained information showing that at Watchet, where the cliffs average 50 feet in height, the sea has gained at least 200 yards during the last 150 years. He also showed that at Weston-super-Mare the sea is converting the slopes into cliffs, and he concluded with a notice of the caves and raised beaches near that town.

5. " On the two Plains of Hertfordshire and their Gravels." By T. M'K. Hughes, Esq., M.A., F.G.S.

The high ground near Hertford Heath, Brickenden, &c. forms the higher of the two plains which Mr. Hughes described ; out of it a great valley has been excavated, the bottom of which forms the lower plain ; and out of this, again, the valleys of the existing streams have been scooped.

The gravels of the upper plain are a marine deposit, and indicate a marine denudation of great antiquity, followed by an emergence, during which the old valleys were scooped out of that plain. The gravels of these valley-plains were formed during a subsequent submergence ; they contain bands of clay and loam passing into Boulder-clay, and are probably marine. This submergence continued until the Boulder-clay was deposited on the top of the higher-plain gravels ; and then succeeded a period of emergence, during which the present valleys were scooped out of the lower plain.

XXXVIII. *Intelligence and Miscellaneous Articles.*

ON THE DURATION OF INDUCTION-CURRENTS.
BY P. BLASERNA.

IN the theory of induction-currents it has hitherto been generally allowed—

(1) That they are formed at the very instant the primary circuit is closed or opened.

(2) That their duration is infinitely small.

I endeavoured to verify these two points experimentally by means of a rotating apparatus, the construction of which is like that which M. Guillemin used in his researches on the propagation of the current of the battery, and also like that which M. Hipp used in his experiments on the velocity of induction-currents in the great telegraphic lines.

Two wooden cylinders, A and B, 8 centims. in diameter and 1 centim. in length, were fixed on the same axis, which could be rotated with a velocity of from 20 to 150 turns in a second. On the circumference of the cylinder A a brass plate was let in which occupied about half the circumference (almost 180°); on that of the cylinder B there was also a very thin brass plate which represented a degree of the circumference. To vary the conditions, I had several spare cylinders with larger and smaller plates. To each cylinder there was firmly fixed a cylinder (*a, b*) of much smaller diameter, made of boxwood and entirely covered with brass. Thus the whole apparatus consisted of the small cylinder *a,* of the cylinders A and B, and of the small cylinder *b* arranged on the same axis, and with a good metallic contact between *a* and A, and between B and *b*. Four metal springs rested against these four cylinders to break or make contact. They were pressed by paper cushions, which stopped the vibrations.

The primary current, furnished by several Bunsen's elements, passed by a commutator, by the thick wire of a small induction-coil (without a contact-breaker), through a tangent-compass, by the springs of the cylinders *a* and A, and returned to the pile. It was thus opened or closed according as the spring A rested on the wooden cylinder or on the brass plate. The induction-current was then formed in the coil, passed by the springs B and *b*, then through a very sensitive galvanometer, and then back to the coil. It was measured on the galvanometer. By varying the velocity of rotation, and giving to the plate in B any position whatever behind that of A, the mode of formation of induction-currents could be studied.

I will mention the principal results I have obtained, intending meanwhile to continue my researches with a much more perfect form of apparatus, which I am now constructing.

(1) The moment the primary current is opened or closed, an induction-current is formed. The time which elapses between the closing or opening of the principal current and the moment at which the induced current is produced is so small that I have not been able to determine it. In any case it is less than $\frac{1}{50000}$ of a second.

(2) But at this moment the induced current is not terminated; it still increases, then diminishes pretty rapidly, and continues for a certain time, becoming very weak.

(3) The total duration of the induced current is always appreciable. In some cases I have observed a feeble current as much as $\frac{1}{200}$ of a second after the primary current was closed; and it is probable that it lasts even longer.

If we wish to represent graphically the induced current, taking the times for abscissæ and the corresponding intensities for ordinates, we have a curve formed, for times less than $\frac{1}{50000}$ of a second, of a straight line almost perpendicular to the axis of the abscissæ, which curves while still ascending, soon attains a maximum, then rapidly descends, and, after bending indefinitely, approaches the axis of the abscissæ without its being possible to fix exactly the point at which it becomes merged in this axis. In any case this point corresponds to an appreciable time.—*Comptes Rendus,* July 29, 1867.

ON THE PASSAGE OF ELECTRICAL CURRENTS THROUGH INCANDESCENT GASES. BY M. E. BECQUEREL.

M. E. Bouchotte has recently observed the interesting fact that when a voltameter containing acidulated water is introduced into the circuit of a magneto-electrical machine which gives two series of alternating currents, one current only circulates, or rather only the currents which are in one direction predominate. To obtain this result, it is sufficient if one of the electrodes be merely a fine platinum wire just dipping into acidulated water, so as to be surrounded by a luminous sheath; this electrode is positive, and the currents which correspond to this electrical arrangement are the only ones which can be perceived.

Having witnessed these effects, I thought it was possible to account for them on the supposition of the unequal electrical conductivity of vapours and incandescent gases, according to the relative magnitude of the electrodes and according to the direction of the currents. I observed, in fact, in 1853 *, that, starting from a red heat, gases become conductors of electricity, and that, in the case of air, when I used as electrodes a platinum tube and a platinum wire stretched along the axis of the tube, and when the electrical tension was equal, the conductivity was greater when the central wire was positive than when it was negative. The luminous sheath in the above experiments, being formed of incandescent gaseous matters, serves as conductor, the surrounding liquid and the central wire forming the two electrodes.

With acidulated water the positive wire should give rise to the maximum conductivity, since one series of currents quite preponderates over the other.

If, as I imagine, the phenomenon may thus be explained, to ac-

* *Annales de Chimie et de Physique,* vol. xxxix. p. 371.

count for the fact that certain liquids give currents in which the wire surrounded by a luminous sheath becomes negative, or rather that they transmit simultaneously, but in unequal proportions, the two systems of inverse induced currents, it is necessary that the conducting-powers and the effects which take place at the passage of the current through the electrodes and the gaseous matter change with the nature of the gaseous matter. M. Bouchotte has observed that the light produced when the currents pass thus between a fine platinum or iron wire was more or less brisk ; with chloride of magsium, more especially, the light is very brilliant, and indicates a polar decomposition of the salt, as well as the presence of this compound in the spark.

The same luminous effects may be observed with an ordinary induction-coil when a rapid succession of sparks are made to strike between a positive platinum wire and a liquid containing an easily decomposable salt, like chloride of sodium, of potassium, calcium, strontium, copper ; and then the sparks are coloured so as to exhibit the characteristic shades observed with saline substances volatilized in flames. This effect is so definite that, by arranging small tubes of 10 to 15 millims. in diameter containing various aqueous saline solutions, and producing, by means of an induction-coil, a very rapid succession of sparks which form a kind of arc between the point of the platinum wire (which is suitably insulated from the glass tube) and the surface of the liquid, we may, by means of a spectroscope, observe the nature of the substances dissolved.

To make the experiment with facility, a tube closed at the bottom has a platinum wire fused in, so as to connect the liquid (which half fills the tube) with one end of the induced wire ; another platinum wire is placed in a capillary tube and projects below it to the length of about a millimetre ; this is then so placed that 'the end of the wire is only a few millims. above the surface of the liquid. To observe the effects, the insulated external wire should be positive and the liquid negative, that being the condition which gives the maximum action. If the sparks pass in the opposite direction, when once the wire is scraped no similar effect is produced, or at any rate a more feeble one. It is possible that the solution undergoes an electrochemical polar decomposition, and that at the surface of the liquid the basic substances decomposed colour the sparks.

These results give an easy means of recognizing by optical analysis, otherwise than by means of coloured flames, the nature of certain saline substances contained in solutions which conduct electricity. —*Comptes Rendus,* December 30, 1867.

ON THE WOODWARDITE OF CORNWALL. BY M. F. PISANI.

Among the new minerals recently discovered in Cornwall, Mr. Church* has described a substance which he calls Woodwardite. It

* Journal of the Chemical Society, vol. iv. p. 130.

forms on killas amorphous crests of a greenish-blue colour, with a waxy surface, and about 5 to 8 millims. in diameter. Its composition is as follows :—

$$
\begin{array}{ll}
\text{Cu O} \ldots\ldots\ldots\ldots & 46\cdot87 \\
\text{SO}^3 \ldots\ldots\ldots\ldots & 12\cdot50 \\
\text{Al}^2\text{O}^3 \ldots\ldots\ldots & 17\cdot66 \\
\text{HO} \ldots\ldots\ldots\ldots & 22\cdot86 \\
\hline
& 99\cdot89
\end{array}
$$

According to the formula assigned by Mr. Church to this substance, it is a sulphate of copper associated with a hydrate of the same base along with a hydrate of alumina.

Having this year received from Mr. Talling, to whose researches we owe the discovery of several interesting minerals in Cornwall, a substance found under the same conditions of deposit as Woodwardite, and strongly resembling it in aspect and texture, though of a brighter green colour, I thought it interesting to make a comparative study of this mineral with that described by Mr. Church.

The qualitative test gave, besides the elements of Woodwardite, a quantity of silica sufficiently great to produce a jelly with concentrated hydrochloric acid ; but the colour of the solution shows that it contains much less copper.

I thought thence that Woodwardite was not a well-defined mineral, but merely a mixture in varying proportions of a subsulphate of copper with a hydrate of alumina. Yet on examining for silica, I found it in a quantity too small to constitute a silicate with alumina.

An analysis of Woodwardite gave me the following numbers :—

		Oxygen.	Ratio.
Oxide of copper	46·8	9·4	4
Sulphuric acid	11·7	7·0	3
Alumina	13·4		
Silica	1·2		
Water.			

The ratio of the sulphuric acid and the oxide of copper are as 3 : 4. This is the same as that I gave for Langite.

The following is the result of the analysis of the new mineral resembling Woodwardite :—

		Oxygen.	Ratio.
Oxide of copper	17·4	3·52	4
Sulphuric acid	4·7	2·82	3
Alumina	33·8		
Silica	6·7		
Water	38·7		
	101·3		

It will be seen from this analysis that the quantity of alumina does not correspond to that found in Woodwardite, while the quan-

tities of sulphuric acid and of oxide of copper are proportionally the same; we may thus consider the new mineral a mixture of Langite ($4\,CuO,\ SO^6 + 4HO$) with a very basic silicate of alumina analogous to Scarbroïte or to Schrötterite (varieties of allophane), or with a hydrate of alumina mixed with a silicate of the genus allophane or Halloysite. Woodwardite is to be considered an analogous mixture, in which there is a hydrate of alumina with a little silica in the place of a very basic allophane.

The Langite found in Cornwall as killas must then, under certain circumstances, have been deposited along with a hydrate of alumina or a very basic silicate to form those mixtures of a variable colour which constitute Woodwardite and the mineral which resembles it.

It must be concluded from these facts that Woodwardite can in no way constitute a new species; and just as we frequently see in various localities allophanes coloured by more or less oxide of copper, there are also in Cornwall allophanes or hydrates of alumina mixed with Langite, as is the case with the two minerals I have examined. Moreover, the quantity of silica in the allophanes being very variable (10 to 24 per cent.), nothing militates against the supposition that the varieties poor in silica contain a mixture of hydrate of alumina, which predominates in Woodwardite, the allophane of which would have a minimum of silica,—completing thus the analogy of the two minerals which form the subject of this note.—*Comptes Rendus,* December 30, 1867.

DIALYSIS OF INDUTION CURRENTS. NOTE BY M. BOUCHOTTE.

We have already* called attention to the remarkable fact that the introduction of a voltameter, containing acidulated water, into the circuit of a magneto-electrical machine gives rise to very marked phenomena of polarization; that to obtain this result it is sufficient to use as electrodes platinum wire sufficiently fine; that one electrode, being immersed to a depth of from 7 to 8 millimetres in the liquid, the other being completely submerged, becomes surrounded by a luminous sheath, and acquires positive electricity.

To regulate more easily the contact of the platinum wire and the liquid, the electrode may be introduced into a glass tube, in which it is made to slide, the metal outside the tube being alone exposed to the electric action. By this arrangement, all the parts of the voltameter may be tested; and it can be shown that the effects of the polarization of the current are independent of the position of the electrodes.

Continuing these researches, the following results have been obtained :—

1. When a second gas-voltameter is brought into the circuit, it yields hydrogen and oxygen gases in the proportion of 2 to 1,—

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* Phil. Mag. Feb. 1868.

showing thus that the electrolytic decomposition which takes place is under the conditions which characterize the ordinary voltaic pile, or a magneto-electrical machine with adjusted currents.

In a sulphate-of-copper voltameter, metal is dissolved at one pole, while copper is deposited electro-chemically at the other.

2. In the dialyzing voltameter, acidulated water is not essential for the production of the phenomena. Most salts we have used modify the normal action of alternating currents; but all of them possess the property of rectifying the extra currents of one series.

The use of a solution of chloride of magnesium gives rise to a light of the greatest beauty. The electrode, which is immersed to a depth of a few millimetres, immediately becomes covered with metallic magnesium, which is at once burned with the production of a bright light. In this experiment, the platinum wire may be replaced by one of iron, which then itself burns slowly, increasing the power of the light; in spite of that, if the iron is placed gradually in the liquid, its combustion is slow enough to obtain a very constant luminous effect.

After having studied these special properties of induction-currents by the aid of a magneto-electrical machine having high tension, it was necessary to ascertain if the same phenomena could be produced by the aid of a source of electricity having smaller electromotive force. With this view we used a Nollet's machine with eight coils, like the preceding, but surrounded by a wire having but a small resistance. This machine has an electromotive force equal to 22 elements of sulphate of copper.

When the dialyzing voltameter contained acidulated water, the absorption of one series was also affected. But we have obtained effects of quantity far more intense by using as the liquid a solution of bichloride of mercury in salt water. In this case more of the wire which acquires positive electricity may be immersed in the liquid; the resistance is thereby diminished.

At the commencement of the experiment protochloride of mercury is formed, which soon after dissolves under the influence of the liberated chlorine. From this moment the mercury is seen to form round about the electrode, and separates when a pretty large globule is formed, while the current acquires an intensity the measurement of which will be afterwards given. The liquid of the voltameter acquires a higher temperature under the action of the currents. If the position of the electrode be not properly regulated, a moment is reached at which the two currents retain their normal properties, and then the needle of the galvanometer is no longer deflected; but by suitably arranging the position of the electrode in the voltameter, it may easily be retained in a liquid medium at a convenient temperature.

Adopting this method, and causing the system to act upon a bath of sulphate of copper, we succeeded in obtaining from 7 to 8 grammes of electrolytically deposited copper in an hour.

The passage of the currents in a Ruhmkorff's coil deserves special attention.

The contact-breaker being suppressed, Nollet's apparatus produces in the induced wire effects of tension which are so weak that a spark of $\frac{1}{4}$ millimetre in length is with difficulty obtained. But on introducing into the circuit the dialyzing voltameter, the aspect of the experiment is changed. A spark, several centimetres in length, is obtained; the induced current passes in M. E. Becquerel's tubes, as well as in those of Geissler, so long as one set of currents retains an action which is independent of the other series. The poles in the tubes are well marked. But if the conductivity of the dialyzer be increased, all the currents pass with their normal properties, and act simultaneously on the coils.

It would appear to follow from these facts, that the introduction of the dialyzer into the circuit gives rise to the extra currents of either one series or the other, or to both, at the will of the operator.

We may, in any case, say that the dialyzer applied to Ruhmkorff's coil acts as perfectly as the best contact-breaker. It must be added that, if it is not desired to absorb one series of the currents, all liquids which are good conductors are equally suitable.

In order to obtain an approximate value for the effects of the dialyzing voltameter, we introduced into the circuit a Bunsen's element, which, by means of the commutator, could act first in the direction of the currents of the machine, and afterwards in opposition to them.

In the first case, a sine-compass indicated a deflection of 31 degrees, the sine of which $=5\cdot5$; in the second, a deflection of 20 degrees, the sine of which is $3\cdot42$. From this we get the number 5 as the ratio between the electromotive force of the series of currents and that of a Bunsen's element.

We have seen above that the electromotive force of the magneto-electrical machine, with a thick wire, represented that of a battery of 22 sulphate-of-copper elements, the effect of which, according to M. Becquerel, is equal to that of $13\frac{1}{2}$ Bunsen's elements. From this, the useful effect obtained by means of the dialyzer would be $\frac{50}{135}$ of that which could be expected from the adjustment of the currents.

New experiments which are in progress may perhaps modify this conclusion a little. We may, however, say that, whenever the operator is desirous of arranging an economical motor at the risk of losing the useful effect of magneto-electrical machines, it will be to his interest to dispense with the adjustment of currents, requiring as this does a commutator, the use of which is attended with inconvenience.—*Comptes Rendus*, Dec. 9, 1867.

Temperature R.°
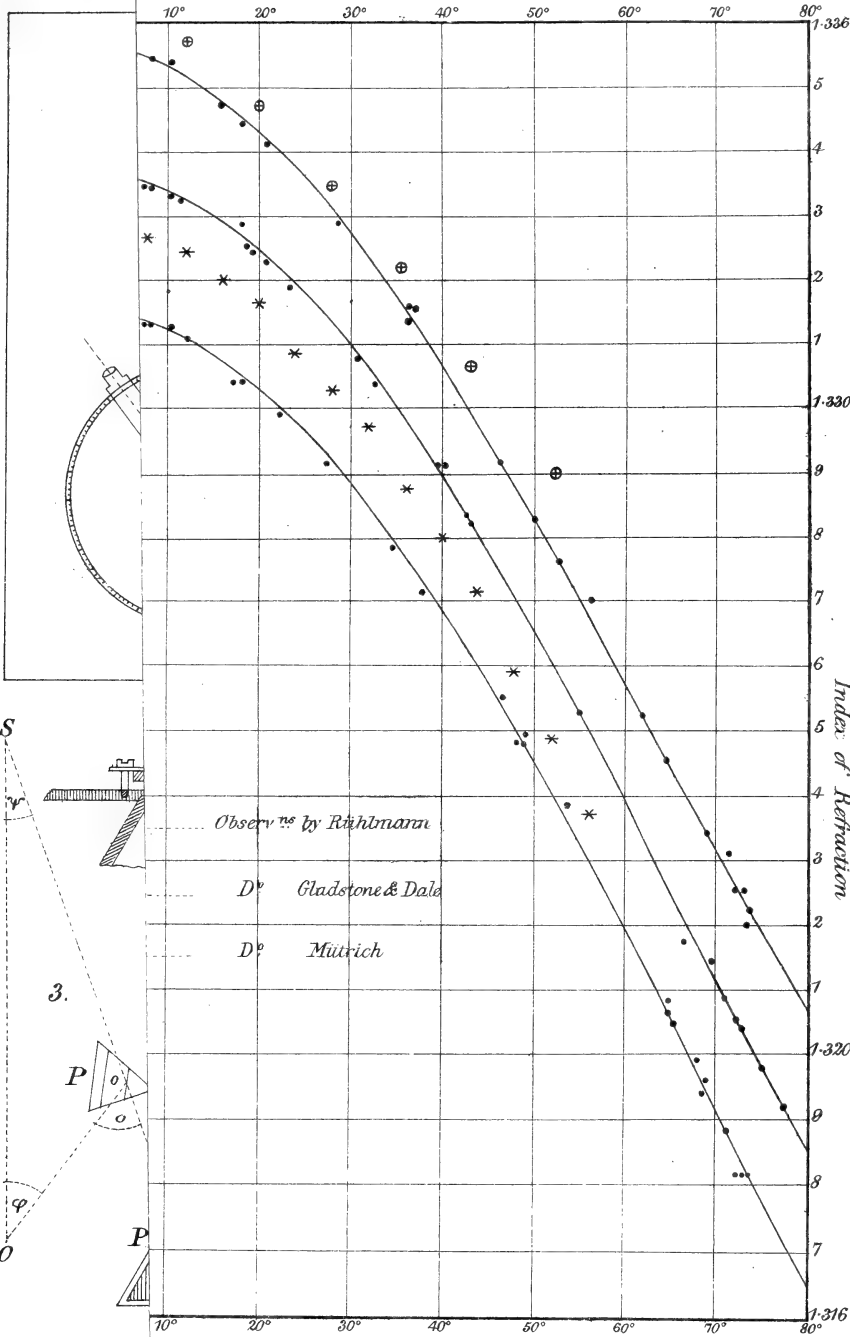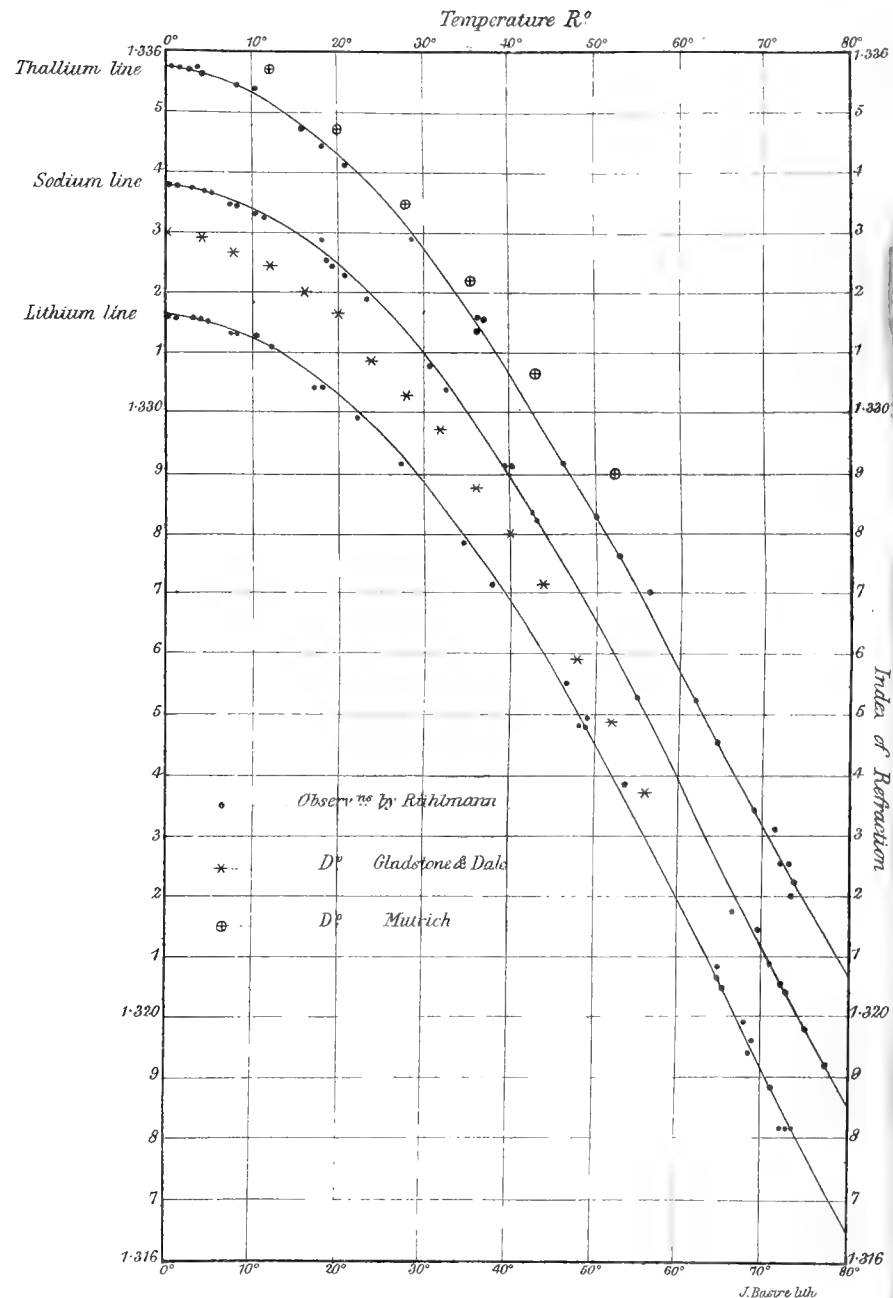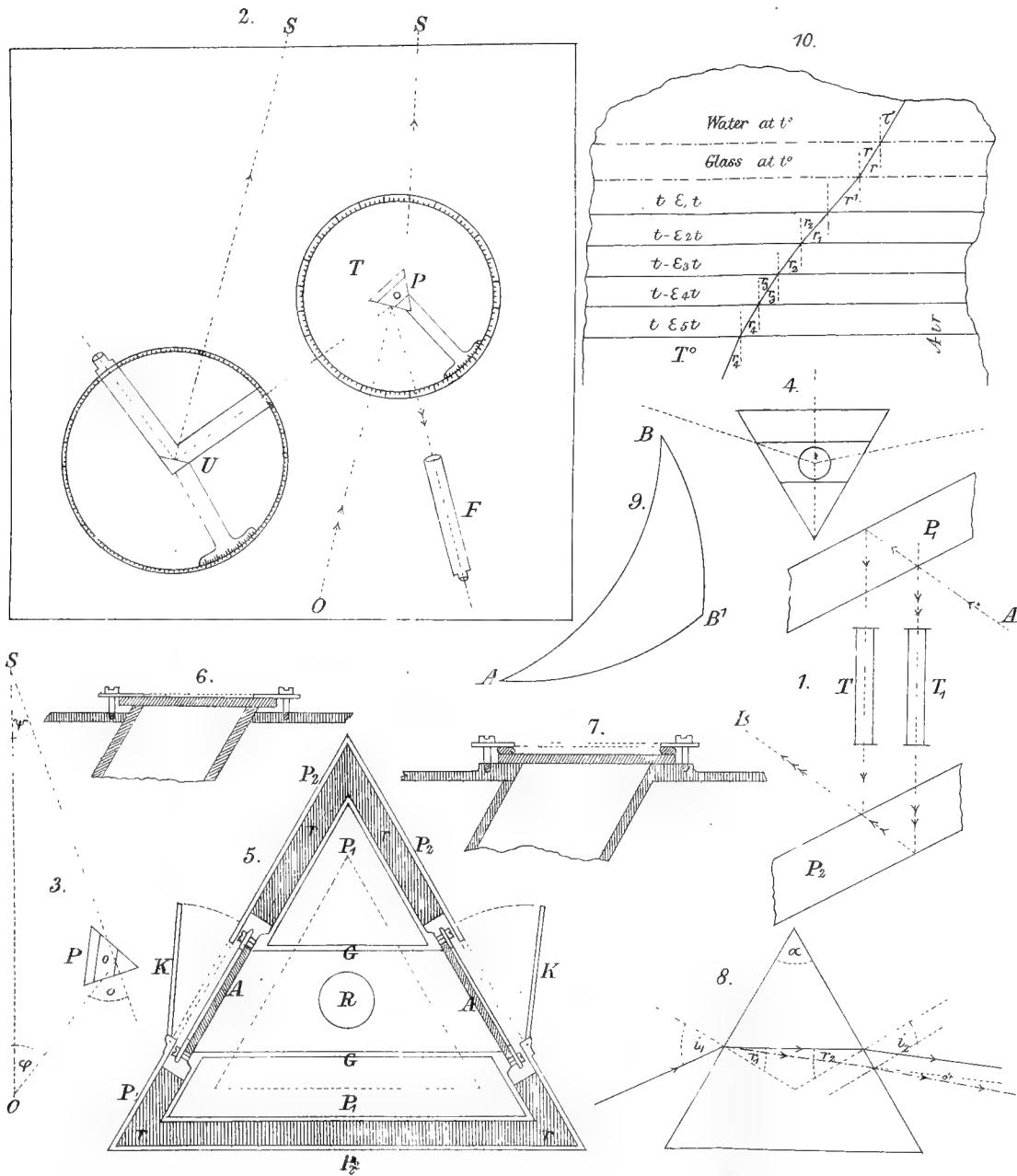
10°   20°   30°   40°   50°   60°   70°   80°

1·336

5

4

3

2

1

1·330

9

8

7

6

5

4

3

2

1

1·320

9

8

7

1·316

Index of Refraction

Observ.ⁿˢ *by Rühlmann*

Dᵒ   *Gladstone & Dale*

Dᵒ   *Müttrich*

3.

S

ψ

φ

O

P   o'
     o

P

10°   20°   30°   40°   50°   60°   70°   80°

J.Basire lith.

XXXIX. *On " Inductive Circuits," or the Application of* Ohm's *Law to Problems of Electrostatics. By* F. C. WEBB, *M.I.C.E.*[*]

PROBLEMS relating to the distribution of electricity on conductors of different shapes, and on conductors and Leyden jars differently grouped, have from time to time formed the subject of mathematical investigation by many able mathematicians. The results of the labours of George Green appear, according to Sir William Thomson, the most important; for Sir William has remarked, in a paper read before the British Association, that " there is no branch of natural philosophy of which the elementary laws are more simple than those which regulate the distribution of electricity upon conducting bodies; yet its impracticability has always been the reproach of the mathematical theory of electricity. . . . . The researches of our countryman, Green, have entirely removed this forbidding aspect from the theory of electricity, and led to the elementary propositions which must constitute the legitimate foundation of every perfect mathematical structure that is to be made from the materials furnished in the experimental laws of Coulomb."

In spite of this great advance, problems of electrostatics in their generality must belong to a very high class of mathematics.

There is a large class of problems of this nature which may, however, be solved by a very simple consideration of the subject and the application of Ohm's formula for conduction. It is not pretended that by this method all such problems can be solved that are soluble by the complete mathematical theory; still, out of the few examples of the application of Green's method

given in his essay, several can be solved by the method the author advocates.

It has for some years past been acknowledged that the accumulation of electricity on the interior surface of the gutta-percha envelope of a submarine telegraph-conductor depends, in a certain manner, on the geometrical dimensions of the envelope and its "specific inductive capacity," and that, by considering the envelope as a conductor in the direction of its thickness, the same formula which expresses its resistance to the conduction of electricity from a given source represents also its resistance to the accumulation of electricity on the surfaces of the envelope, the constant expressing the *specific resistance to conduction* being only altered to one expressing the *specific resistance* to "*accumulation*," "*excitation*," or "*induction*," as the property of the material to facilitate the accumulation on its surface has been variously termed.

Messrs. Siemens, in a paper read before the British Association, 1860, observe, "According to Faraday's conception, the inductive action is communicated (say, from the interior electrified covering of a Leyden jar to the exterior) from atom to atom through the dielectric. In one case the jar is represented by the cable, the inner covering of which is formed by the surface of the copper wire, the exterior by the water."

"The laws which apply to the motion of heat and electricity in conductors are accordingly directly applicable to electro-induction, which may be expressed by the conductivity multiplied by a constant varying with the nature of the insulating material."

In 1861 M. Gaugain, in a note published February 18th in the *Comptes Rendus*, on cylindrical condensers, observes, "It will be seen that in the case, at least, of cylindrical condensers the laws which regulate the propagation of electricity by *excitation* do not differ from those which Ohm has established for propagation by conductibility."

The applications of Ohm's law to problems of electric accumulation seem, however, until September 1861, to have been confined entirely to the problem of a single cylindrical resistance, the formula for which was given by Sir W. Thomson in 1855, Messrs. Siemens in 1859*, and M. Gaugain in 1861, February 18.

In September 1861 M. Gaugain applied it to the case of a spherical condenser, and in the note describing them he observes, "I have indicated in my preceding communication a general principle by means of which all questions relative to condensers

* Page 12, Government Report. This formula does not appear to be correct, perhaps misprinted.

may be transformed into questions of propagation, and thus brought within the domain of Ohm's law. The exactitude of this principle has been already demonstrated experimentally (1) in the case of concentric cylindrical condensers, (2) in the case of excentric cylindrical condensers, and (3) in the case of plane condensers*. I have now verified it for a new class of condensers, that of concentrical spherical condensers."

In all these cases the quantity accumulated on the surfaces of the dielectric would be, with a given source, inversely proportional to the *"resistance"* of the dielectric to accumulation or induction ; and the term *"* inductive resistance*"* has been very frequently employed to express this resistance, in opposition to *"* conductive resistance."

In all these examples hitherto mentioned, the source of electric generation is supposed to have one pole connected to one surface of the condenser, whilst the other pole is in connexion, through the earth or otherwise, with the other surface. A single resistance exists ; and the *quantity accumulated on the surfaces* is inversely proportional to this resistance, in the same way that, if in the galvanic circuit a single resistance exist, *the quantity passing a single section of the circuit in a given time will be inversely proportional to the resistance* thus supposed to form the whole resistance of the circuit.

When both poles of the source are connected to conductors insulated from one another and from the earth, new and interesting problems arise. The quantity on either conductor will evidently be no longer simply inversely proportional to the inductive resistance, separating it from the earth or nearest conducting surface ; for in such case, with two conductors of different dimensions attached to the poles of a source, we should have unequal quantities of electricity generated at the two poles—an acknowledged impossibility.

If, however, we consider that, just as for conduction to take place in the conductive circuit there must be a continuous chain of conducting matter from one pole to the other, so for accumulation to take place we must have between the poles of the source a continuous chain or series of inductive bodies (or inductive resistances) joined, it is true, by conductors, we shall find the means, by applying Ohm's law for the conductive circuit to what may be termed the *"inductive circuit,"* of solving this and many other problems.

We have, in fact, only to trace the inductive circuits that exist even to branch or derived circuits, and apply the formula for conductive circuits. Thus in the case of a single pair of flat plates (fig. 1), a single Leyden jar (fig. 2), or the spherical shell inves-

* *Comptes Rendus*, February 18, April 29, and June 17, 1861.

tigated by M. Gaugain (fig. 3), we have inductive circuits formed of a single resistance in each case ; and the quantities that can be
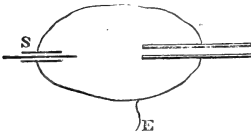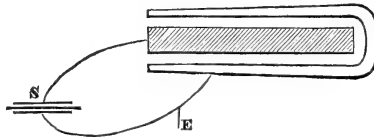
Fig. 1.   Fig. 2.   Fig. 3
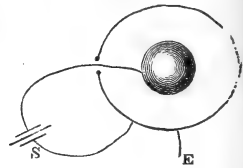
accumulated from a given source on the two bounding surfaces of the dielectric composing this resistance will be equal and opposite in name, and inversely proportional to the resistance thus forming the whole inductive resistance of the circuit.

When both poles are connected to insulated conductors, then *two* or *more resistances* exist in the circuit ; and as in the *conductive* circuit the quantity passing any section in a given time (*i.e.* the "magnitude," "intensity," or "quantity" of the current) is *inversely proportional to the sum of all the resistances in the circuit*, so in the " inductive circuit " the *quantity that will be accumulated on any one surface of the resistances will be inversely proportional to the sum of all the inductive resistances of the circuit.*

Thus, if S be a source, one pole of which is connected to a flat plate A, and the other to the plate B, and D and C be two plates joined by a conducting wire, then we have an inductive circuit having two resistances, viz. the dielectric separating D from A, and that separating B from C. The quantity on each of the plates will be the same, notwithstanding that one set of plates are larger and closer together than the other, but

Fig. 4.

opposite in name on each successive plate ; and this quantity will be inversely proportional to the *sum of the two resistances.*
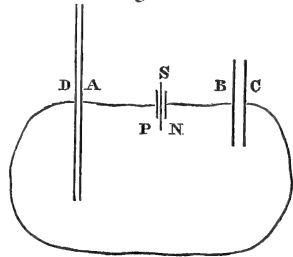
In the same way two Leyden jars of different sizes, or two submarine cables of different lengths, attached to the two poles of a source, will contain equal quantities ; and that quantity can be determined by the simple formula for conduction,

$$Q = \frac{E}{R+r},$$

where Q is the quantity in either jar or cable, and R and r the inductive resistances of the jars or cable.

Thus, if the plates are supposed equal and equidistant at first,

and we take as unity the quantity that would be accumulated on one set of plates, supposing them at first to constitute the only resistance of the circuit, then, when the two sets are placed in circuit, since the resistance of the whole circuit is doubled, the quantity on each plate would be only 0·5 ; and if now the resistance of one set be increased by doubling the distance between them, the quantity would be reduced to 0·33.

By the same means the quantity that would be accumulated on a series of several pairs of equal plates joined "in cascade" may be found, and compared with the quantity that would be accumulated on a single pair ; and it will be seen that, as the resistance of m sets of plates will be m times as great as that of one, the quantity accumulated on each set of plates will be m times smaller than that which it would be with one set of plates. But as there are m sets of plates thus charged, the total quantity generated and accumulated is the same as if one set of plates only were employed. This agrees with the result of Green's investigation of the same problem, and is thus enunciated by Green :—"The total quantity of electricity contained in the interior of any number of equal and similar jars*, when one of them communicates with the prime conductor, and the others are charged *by cascade,* is precisely equal to that which *one only* would receive if placed in communication with the same conductor, its exterior surface being connected with the common reservoir " (that is to say, in connexion through the surrounding objects or the earth with the other pole of the source of generation).

When one set of surfaces of two or more Leyden jars or other inductive resistances are connected as parallel branch resistances to one pole of a source, the other pole of which is connected either directly or through the surrounding conductors to the other surfaces of such resistances, the quantity that will be accumulated on the surface of any one resistance is quite independent of the magnitude of the other resistances thus grouped. This case has no parallel in the *conductive* circuit, at least in a galvanic circuit ; and the difference arises from the fact that in the galvanic circuit we have always the resistance of the battery as a resistance common to all the branches, whereas in an inductive circuit the resistance of the battery is a conductive and *not* an inductive circuit. If in an inductive circuit we have a resistance (A) common to both of two or more branch resistances (B and C), as in figs. 5 and 6, then this indifference of the branch resistances to one another disappears, and none of the resistances can be altered without affecting the quantity that will be accumulated on each. The formula for these I have already published,

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* This is not strictly correct as regards *jars.* The reason of this is explained further on.—F. C. W.

and it is not necessary to recapitulate its applications here. The following problem, however, is new, and is a good example

Fig. 5.
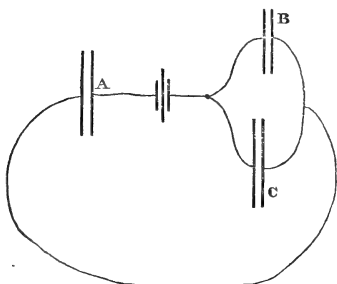
Fig. 6.
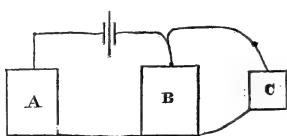
of the mode of treating electrostatics by means of the theory of inductive circuits, and shows the relation that exists between quantity, density, tension, and inductive resistance. If two conducting spheres, A and B, are connected to opposite poles of a source, then an inductive circuit will be formed the resistances of which consist of the dielectric separating the surface of each sphere from the

Fig. 7.

nearest surrounding conductors. If the surrounding objects are distant, these resistances are inversely proportional to the radii of the spheres. Consequently if we call r the radius of A, and r' the radius of B, and represent by R the sum of the inductive resistances of the circuit, we have
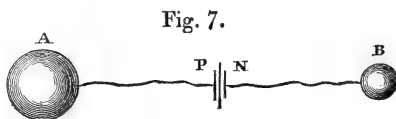
$$R = \frac{1}{r} + \frac{1}{r'};$$

and since the quantity generated on any one surface of the inductive circuit is inversely proportional to R, we have

$$Q = \frac{E}{\frac{1}{r} + \frac{1}{r'}}.$$

Thus, if we call that quantity unity which would be accumulated on a sphere whose diameter is one, where one pole of the source is connected to surrounding objects or " to earth," then Q in the above equation would express that which would be accumulated on each sphere when their radii are r and r'.

Now I have shown elsewhere that the tension of the electricity on each sphere to surrounding objects or earth, or the electric potential of each sphere, is proportional to the quantity on

the sphere multiplied by the inductive resistance that separates that sphere from surrounding objects, or $T = QI$, where $T =$ tension to the earth as datum, $Q =$ quantity of electricity on the sphere, and $I =$ inductive resistance separating the sphere from surrounding conductors connected to earth. This expression gives a perfectly definite meaning to the term tension, which has often before been used in a vague sense. And since I is proportional to $\frac{1}{r}$ and $\frac{1}{r'}$, we have

$$T = \frac{1}{r} Q = \frac{Q}{r} \text{ for the tension of one sphere,}$$

and $$T' = \frac{1}{r'} Q = \frac{Q}{r'} \text{ for the other sphere.}$$

And since the density is proportional to the quantity divided by the surface over which it is distributed, or $D = \frac{Q}{S}$, we have

$$D = \frac{Q}{r^2} \text{ for the density on one sphere,}$$

and $$D' = \frac{Q}{r'^2} \text{ for the density on the other.}$$

The attached Table gives a few of the calculated values of Q (the quantity), D and D' (the densities), and T and T' (the tensions) for a few values of r and r',—the quantity, density, and tension, when one sphere of unit radius is attached to one pole and the other pole is connected to surrounding conductors (or to earth), being taken as unity of quantity, density, and tension respectively.

No.	r.	r'.	R. $\frac{1}{r} + \frac{1}{r'}$.	Q. $\frac{1}{R}$.	D. $\frac{Q}{r^2}$.	D'. $\frac{Q}{r'^2}$.	T+. $\frac{Q}{r}$.	T'−. $\frac{Q}{r'}$.
1.	1	1	2	0·5	0·5	0·5	0·5	0·5
2.	1	2	1·5	0·66	0·66	0·165	0·66	0·33
3.	1	3	1·33	0·75	0·75	0·083	0·75	0·25
4.	2	2	1	1	0·25	0·25	0·5	0·5
5.	2	3	0·83	1·2	0·3	0·133	0·6	0·4
6.	3	3	0·66	1·5	0·166	0·166	0·5	0·5
7.	1	100	1·01	0·99	0·99	0·000099	0·99	0·0099

The method of considering problems of electrostatics by means of inductive circuits, I submit, explains many of the phenomena of electrical experiments hitherto unexplained, or at least very imperfectly explained. Thus, if an electrical machine has its rubber insulated, it is well known that but little accumulation takes place on

the prime conductor. The reason of this is easily seen when we consider the problem by means of the theory of inductive circuits. The resistance of the circuit is now increased by the resistance of the dielectric separating the rubber from surrounding objects; and as the rubber has little surface compared to that of the prime conductor, this resistance is much greater than that existing between the surface of the prime conductor and the surrounding objects, so that the resistance of the whole circuit is thus increased considerably more than double,—the exact amount of the increase depending, however, on the proportion of the rubber to the prime conductor and the proximity of surrounding conductors to it.

If the rubber is connected to surrounding objects, the only resistance in the inductive circuit consists of the dielectric separating the surface of the prime conductor from the surrounding conductors. The quantity generated is therefore much greater than when the total resistance included that between the rubber and surrounding objects. The total quantity of positive generated is accumulated on the prime conductor, and the equal quantity of negative passes to surrounding objects, and there remains until neutralized by recombination with the positive on the conductor.

In the same way, if we connect the rubber to the interior of a Leyden jar, and the prime conductor to the interior of another jar of equal size, the exterior of both jars being in connexion, we shall be able to accumulate in each about half the quantity that would be accumulated in a single jar with the rubber connected to the exterior coating. The resistance between the prime conductor and surrounding objects and that between the rubber and surrounding objects form here two branch resistances, and these, being unequal, cause a slight inequality in the jars ; that jar connected to the prime conductor will therefore contain a little less than the jar attached to the rubber.

With a voltaic battery and two or more variable lengths of submarine cable the laws of inductive circuits are best seen. Thus, if a battery has one pole insulated and the other pole connected to a long length of cable, say a hundred miles, having its distant end insulated, no charge in the cable will take place. The resistances here consist of the envelope of the cable and of the resistance separating the insulated terminal from surrounding objects. This resistance is practically infinite ; and hence no generation. If, now, a mile length be placed in contact with the previously insulated pole, certain equal and opposite quantities will be generated at each pole and charge the cables equally. If the short length is increased, the quantity that will be generated will be increased according to the formula

$Q = \dfrac{E}{r + r'}$; and when the two lengths are equal, the quantity in each will be half that which would be accumulated in one, if the other pole were connected to earth.

In the charging of a series of Leyden jars arranged in cascade (fig. 8), with the last jar connected to earth, the reason that the accumulation in each jar is not quite equal, but is less in each jar nearest the earth connexion than in the preceding one, is easily seen by considering the problem as one of branch circuits. The first jar in a cascade of two jars is a resistance common to both

Fig. 8.
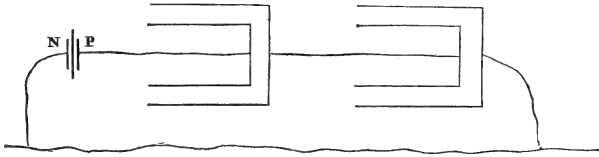
branches; and the branches consist, first, of the dielectric intervening between the outer armature of the first jar and the surrounding conductors, and, secondly, of the glass of the second jar.

The quantity in the first jar must be equal to the quantity on the outside of the outer coating of the same jar (or what is sometimes termed the " free electricity ") added to the quantity in the second jar, just in the same way that the current in any part of a conductive circuit (containing a branch) must, before bifurcation, be equal to the sum of the currents in the two branches after bifurcation. The quantity in the second jar will be therefore less than that in the first by exactly this quantity of " free electricity " on the outside of the first jar. And as this quantity can be increased by lessening the resistance of this branch of the circuit, as, for instance, by approaching conductors to the outside of the jar, it follows that the disproportion in the charges of the jars will depend on the proximity of surrounding conductors to the whole series.

Many other problems can be thus considered and explained, and, where the inductive resistances are defined, worked out by the formula; so that what will occur in cases hitherto never before treated, can be accurately foretold. Moreover it will be seen that all the most ordinary phenomena in electrical experiment regarding generation and accumulation can be explained without any recourse to the earth as a " common reservoir."

In a future communication I propose to detail some experiments with submarine cables grouped to the two poles of a battery, in illustration of the subject.

XL. *On a new form of Voltameter and Voltastat.* By FREDE-
RICK GUTHRIE, *Ph.D., F.R.S.E., Professor of Physics and
Chemistry, Royal College, Mauritius**.

THE instrument described below may be advantageously used
when a galvanic current of great
constancy is required for a considerable
time. When interposed in a circuit it
allows a certain quantity of the cur-
rent to pass, and it measures the amount
which passes. Its construction and use
are the following:—

A is a wide test-tube on a foot.

B is mercury.

C is dilute sulphuric acid.

D is a long tube, open at both ends,
passing through the cork M and dip-
ping under the mercury.

E is a tube passing through the cork
and open below; it carries a bulb, N,
containing fragments of linen. The
upper end is closed, with the exception
of a microscopic opening, F.

H and I are the electrode wires, pro-
tected by glass tubes where they pass
through the cork.

K and L are platinum electrodes, in
the shape of narrow strips of foil con-
verging towards the top, and kept apart
at top and bottom by strips of glass
fused on to the platinum.

G is a little test-tube which serves to
protect the end of the tube E from dust.
It is separated from E by fragments of
linen.

The only point requiring particular
attention is the formation of the capil-
lary opening F. This opening is best
made by blowing a little bulb at the end
of the tube, bursting a little hole in this
before the blowpipe, and allowing the
whole to collapse while the air is conti-
nually injected. Several such tubes
should be prepared. It is not difficult
in this way to get an opening in D so
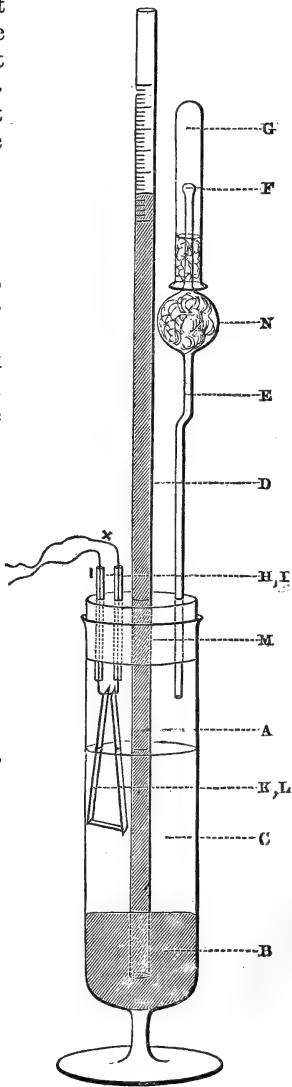
* Communicated by the Author.

extremely small as not to allow the mercury, when at the top of D, to fall in less than ten minutes or a quarter of an hour. The cork and top of the tube C are made perfectly airtight by sealing-wax.

On connecting H and I with the poles of a battery, the water in C is decomposed; the detonating gas can only escape by the opening F. The hindrance it meets with on account of the small size of F causes it to force the mercury up D. The effect of the rise of the mercury in D is twofold; it forces more gas through F, at the same time that it lays bare a part of the electrodes, leaving the active portions of them further apart. The quantity of gas produced is accordingly diminished. In other words, an increase in the strength of the current produces effects which diminish the strength of the current. The instrument is a regulator, which may be compared with the governor of a steam-engine.

It is found that the mercury rises to a certain height in D, and remains nearly at that height for many hours. Since a certain height of the mercury in D corresponds to a certain pressure in the interior, and since the latter corresponds to a certain rate of delivery through F, it follows that the quantity of electricity passing through the instrument is directly measured by the height of the mercury. The actual relation between the height of the mercury and the electricity which passes may, of course, be measured either by interposing a galvanometer or actually measuring the quantity of gas evolved by fitting a gas-delivery tube over F, &c.

Nevertheless an exceeding gradual depression in D must occur even with a perfectly constant current, on account of the removal of a portion of the liquid C by electrolysis. For many purposes this is negligible, namely when the instrument is used as a voltastat. It is clear that, as a certain height in D corresponds to a certain activity, the amount of water lost from C in a given time is measured by the height in D. Hence, on knowing the relative diameters of D and A, and knowing the amount of water decomposed in a given time, a simple calculation serves to make the minute correction.

London Institution,
   April 3, 1868.

XLI. *Investigation of the Alteration produced by Heat in the Velocity of Propagation of Light in Water.* By RICHARD RÜHLMANN.

IV. *The Measurements.*

THE following scheme was followed in making the observations.

(1) Determination of the angle of the prism at the temperature of observation.

(2) Fixing the minimum deviation for the sodium-line.

(3) Maintenance of the temperature constant and reading of the thermometer.

(4) Measurement of the angle of least deviation.

(5) Measurement of the distances of the axis of rotation of the universal circle from the prism and from the slit.

(6) Determination of the temperature of the place where the observations were made.

The angular measurements (1) were always got by taking, as the most correct value, the mean of a short sequence of observations which were not extended over too great a thermal range.

In order to maintain the temperature constant during the progress of observation, the lamp, after warming the liquid and during the determination of the lines, was either entirely withdrawn or its flame was made exceedingly small. While the outer liquid, which was the warmer, was establishing thermal equilibrium with the inner one and radiation had already begun, there were always some seconds during which the temperature in the liquid remained tolerably constant. This was shown by the refracted images of the spectral lines appearing sharply defined and straight. The position of the lines was then quickly determined and the temperature read off on the thermometer; the minimum deflection was always taken for the sodium-line only; and this position remained unchanged within several degrees of thermal variation; for even considerable deviations from the true minimum had no influence upon the position of the refracted image. Strictly, it would be necessary to calculate the final result according to another formula. As a rule, we have omitted to take this into account here.

If, namely, for a ray D for example, the minimum of the deflection is determined, then the following formula serves for calculation:—

$$\frac{n}{\mathrm{D}} = \frac{\sin \frac{1}{2}(d+\alpha)}{\sin \frac{1}{2}\alpha}. \qquad \cdots \cdots \quad (\mathrm{A})$$

If, now, i_1 and i_2 are the angles of incidence, and r_1 and r_2 the angles of refraction at the two surfaces (see fig. 8), then

$$\sin i_1 = n \sin r_1, \quad \sin i_2 = n \sin r_2, \quad \dots \quad (1)$$

$$r_1 + r_2 = \alpha, \quad \dots \dots \dots \dots \quad (2)$$

$$d = i_1 + i_2 - \alpha, \quad \text{or } i_1 = d - i_2 + \alpha, \quad \dots \quad (3)$$

$$\sin(d - i_2 + \alpha) = n \sin(\alpha - r_2). \quad \dots \quad (4)$$

On inserting the minimum of the deflection, we find

$$i_1 = i_2 = \frac{d + \alpha}{2}, \quad r_1 = r_2 = \frac{\alpha}{2}.$$

Suppose, now, a neighbouring ray with the same position of the prism has the deviation $d - \delta$, its index of refraction being v, and its first angle of refraction being ρ_1. It follows from the invariability of the angle of incidence that

$$\sin \frac{d + \alpha}{2} = v \sin \rho_1. \quad \dots \dots \dots \quad (5)$$

For the second angle of refraction we have

$$\sin\left(\frac{d + \alpha}{2} - \delta\right) = v \sin(\alpha - \rho_1). \quad \dots \quad (6)$$

If, now, we put $\rho_1 = \frac{\alpha}{2} + \beta$ and develope (6), we find

$$\left. \begin{aligned} \sin \frac{d + \alpha - \delta}{2} \cos \frac{\delta}{2} &- \cos \frac{d + \alpha - \delta}{2} \sin \frac{\delta}{2} \\ &= v \sin \frac{\alpha}{2} \cos \beta - v \cos \frac{\alpha}{2} \sin \beta. \end{aligned} \right\} \quad \dots \quad (7)$$

Similarly, from (5) we find

$$\left. \begin{aligned} \sin \frac{d + \alpha - \delta}{2} \cos \frac{\delta}{2} &+ \cos \frac{d + \alpha - \delta}{2} \sin \frac{\delta}{2} \\ &= v \sin \frac{\alpha}{2} \cos \beta + v \cos \frac{\alpha}{2} \sin \beta. \end{aligned} \right\} \quad \dots \quad (8)$$

By the addition and subtraction of (7) and (8) we get the following :—

$$\sin \frac{d + \alpha - \delta}{2} \cos \frac{\delta}{2} = v \sin \frac{\alpha}{2} \cos \beta, \quad \dots \quad (9)$$

$$\cos \frac{d + \alpha - \delta}{2} \sin \frac{\delta}{2} = v \cos \frac{\alpha}{2} \sin \beta. \quad \dots \quad (10)$$

Dividing (10) by (9) we find

$$\cot\frac{d+\alpha-\delta}{2}\tan\frac{\delta}{2}\tan\frac{\alpha}{2}=\tan\beta. \quad . \quad . \quad . \quad (11)$$

Hence β is found, and from formula (B) we get the index of refraction

$$\nu=\frac{\sin\left(\dfrac{d+\alpha}{2}\right)}{\sin\left(\dfrac{\alpha}{2}+\beta\right)}\Bigg\}. \quad . \quad . \quad . \quad \text{(B)} \quad (12)$$

If we perform the calculation for the three data at $0°$ after they have been adjusted to the extent of $10''$, then

$d_{Na}=22°\ 55'\ 5''$, $\delta_{Li}=10'\ 0''$, $\delta_{Th}=-8'\ 20''$, $\alpha=58°\ 38'\ 31''$.

We accordingly find

$$\beta_{Li}=+3'\ 16'', \qquad \beta_{Th}=-2'\ 42''.$$

This introduced into (12) gives

$$n_{Li}=1\cdot33154, \qquad n_{Th}=1\cdot33566;$$

while by the ordinary methods these values are also found :—

$$n_{Li}=1\cdot33154, \qquad n_{Th}=1\cdot33566.$$

The differences are still inappreciable in the fifth decimal place; hence we are perfectly justified in reckoning throughout by means of the more simple formula (A).

The results of observation are collected in the Tables I., II., III. The arrangement had to be altered once, whereby the distances were altered. The measurements made with the first arrangement are marked by an asterisk (*). The column "corrected temperature" contains the temperatures corrected (from $-55°$, the atmospheric temperature being $8°$) for the projection of the scale and the correction of the thermometer compared with the normal thermometer. The columns "angle of least deviation" contain under ϕ the readings of the universal circle, under ψ the corrections on account of the excentric position of the prism, and under δ the proper deviation of the ray. The atmospheric temperature varied, during the whole of the observations (only a few tenths of degrees Reaumur excepted), through $7°$ R. The atmospheric pressure varied between 337 and 330 Paris lines, column of mercury. The observations at $0°$ C. were made by filling the hollow of the prism P_1 with pure melting ice and waiting until no further alteration was observed in the index of refraction.

TABLE I.—Indices of Refraction of Water for the Lithium-line.

Temperature (R.)		Refractive angle, α.	Angle of least deviation.			Index of refraction.		Difference.	
Read.	Corrected.	(° ′ ″)	φ. (° ′ ″)	ψ. (′ ″)	δ. (° ′ ″)	Observed.	Calculated.	Δ.	Δ².
0	0	58 38 31	21 47 35	57 33	22 45 8	1·33155	1·33154	+0·1	0·01
1	1	58 38 31	21 47 23	57 33	22 44 56	1·33150	1·33153	−0·3	0·09
2·9	3·0	58 28 31	21 47 27	57 33	22 45 0	1·33152	1·33152	0	0·00
3·7	3·8	58 38 31	21 47 24	57 33	22 44 57	1·33151	1·33149	+0·2	0·04
4·2	4·3	58 38 31	21 47 22	57 33	22 44 55	1·33150	1·33148	+0·2	0·04
7·7	7·9	58 38 31	21 46 36	57 31	22 44 7	1·33132	1·33134	−0·2	0·04
7·9	8·1	58 38 31	21 46 30	57 32	22 44 2	1·33131	1·33133	−0·2	0·04
*9·9	10·1	58 38 2	21 46 5	57 30	22 43 35	1·33125	1·33123	+0·2	0·04
*12·0	12·3	58 38 2	21 44 15	58 13	22 42 28	1·3311	1·3311	0	0·00
*16·6	17·2	58 37 24	21 42 15	58 8	22 40 23	1·3304	1·33065	−2·5	6·25
17·5	18·1	58 37 24	21 42 56	57 21	22 40 7	1·3304	1·3305	−1	1·00
21·7	22·4	58 38 19	21 40 26	57 16	22 37 42	1·3299	1·3300	−1	1·00
26·9	27·8	58 38 19	21 37 4	57 8	22 34 12	1·3291	1·3292	−1	1·00
34·2	35·1	58 38 3	21 31 25	56 54	22 28 19	1·3278	1·3279	−1	1·00
37·7	38·6	58 38 3	21 28 35	56 45	22 25 20	1·3271	1·3272	−1	1·00
45·3	46·4	58 38 3	21 21 0	56 28	22 17 28	1·32555	1·3254	+1·5	2·25
*47·4	48·5	58 37 55	21 18 20	57 8	22 15 28	1·3248	1·3249	−1	1·00
47·6	48·7	58 38 3	21 18 38	56 21	22 14 59	1·3249	1·3249	0	0·00
47·7	48·8	58 37 55	21 17 30	57 6	22 14 36	1·3248	1·3248	0	0·00
*47·9	49·0	58 37 55	21 17 45	57 6	22 14 51	1·3248	1·3248	−1	1·00
52·4	53·7	58 38 23	21 14 45	56 11	22 10 25	1·3238	1·3239	0	0·00
62·8	64·3	58 38 8	21 1 45	55 40	21 57 25	1·3208	1·3208	0	0·00
63·5	65·1	58 38 8	21 0 40	55 36	21 56 16	1·3205	1·32055	−0·5	0·25
66·2	67·8	58 38 8	20 58 0	55 30	21 53 30	1·3199	1·3198	+1	1·00
67·2	68·8	58 37 55	20 56 35	55 26	21 52 1	1·3196	1·3195	+1	1·00
69·9	71·5	58 37 55	20 53 0	55 15	21 48 15	1·3188	1·3188	0	0·00
71·2	72·8	58 38 12	20 50 22	55 11	21 45 33	1·3181	1·3184	−3	9·00
71·7	73·4	58 38 12	20 50 28	55 10	21 45 38	1·3181	1·3182	−1	1·00
72·1	73·9	58 38 12	20 50 20	55 10	21 45 30	1·3181	1·3181	0	0·00
								ΣΔ² =	29·15

The probable error, w, of one observation is accordingly—

(1) From all observations .... w=0·67 }
(2) For one observation from the series from 0° to 10°... w=0·12 } in units of the fourth decimal place.

Table II.—Indices of Refraction of Water for the Sodium-line.

Temperature (R.) Read.	Corrected.	Refracting angle.	φ	ψ	δ	Index of refraction Observed.	Calculated.	Difference Δ.	Δ².
0°	0°	58 38 31	21 57 5	57 58	22 55 3	1·33375	1·33374	+0·1	0·01
0	0	58 38 31	21 57 9	57 58	22 55 7	1·33380	1·33374	+0·6	0·36
1·2	1·2	58 38 31	21 56 55	57 57	22 54 52	1·33375	1·33374	+0·1	0·01
3·1	3·2	58 38 31	21 56 53	57 57	22 54 50	1·33372	1·33371	+0·1	0·01
3·9	4·0	58 38 31	21 56 41	57 56	22 54 42	1·33271	1·33369	+0·2	0·02
4·6	4·6	58 38 31	21 56 4	57 56	22 54 37	1·33368	1·33368	0	0·00
7·7	7·9	58 38 31	21 56 2	57 55	22 54 59	1·33355	1·33355	0	0·00
7·9	8·0	58 38 31	21 55 55	57 55	22 53 57	1·33353	1·33355	-0·2	0·04
8·1	8·2	58 38 31	21 55 27	57 55	22 53 50	1·33350	1·33354	-0·4	0·16
10·0	10·2	58 38 2	21 53 50	57 53	22 53 20	1·32340	1·33343	-0·3	0·09
*11·4	11·8	58 37 24	21 51 25	58 39	22 52 29	1·3333	1·3333	0	0·00
*18·0	18·4	58 37 24	21 50 30	58 33	22 49 58	1·3328	1·3327	+1	1·00
*18·4	18·8	58 37 24	21 50 10	58 30	22 49 0	1·3325	1·3326	-1	1·00
*19·4	19·6	58 37 24	21 49 45	58 29	22 48 39	1·3324	1·3325	-1	1·00
20·5	20·9	58 37 55	21 49 8	58 28	22 48 13	1·3323	1·3324	-1	1·00
23·2	23·7	58 38 19	21 44 23	57 38	22 46 46	1·3319	1·3319	0	0·00
30·3	30·8	58 38 19	21 42 45	57 26	22 41 49	1·3308	1·3308	0	0·00
32·1	32·7	58 38 3	21 35 50	57 22	22 40 7	1·3304	1·3304	0	0·00
*39·2	39·8	58 37 55	21 35 55	57 53	22 33 43	1·3291	1·3290	+1	1·00
*39·9	39·9	58 37 55	21 33 30	57 53	22 33 48	1·3291	1·3290	+1	1·00
42·2	42·9	58 38 3	21 33 25	56 59	22 30 29	1·3283	1·3283	0	0·00
*42·5	43·4	58 38 23	21 32 10	57 44	22 30 9	1·3283	1·3282	+1	1·00
54·3	55·2	58 37 55	21 21 10	56 28	22 17 38	1·3253	1·3253	0	0·00
66·3	67·7	58 37 55	21 5 33	55 49	22 1 22	1·32175	1·3220	-2·5	6·25
68·2	69·6	58 38 12	21 4 13	55 46	21 59 59	1·32145	1·3214	+0·5	0·25
70·9	72·3	58 38 12	21 2 20	55 40	21 58 0	1·3209	1·3210	-1·0	1·00
71·0	72·4	58 38 12	21 0 40	55 36	21 56 16	1·3205	1·3205	0	0·00
71·4	73·0	58 38 12	21 0 5	55 35	21 55 40	1·3204	1·3204	0	0·00
73·5	75·1	58 37 55	20 57 8	55 30	21 52 38	1·3198	1·31985	-0·5	0·25
75·6	77·3	58 37 12	20 54 55	55 22	21 50 17	1·3192	1·3193	-1	1·00
									ΣΔ² = 16·45

Hence the probable error of one observation—

(1) Judged from all thirty values ...... $w = \mp 0·52$ } units of the fourth decimal place.
(2) from values between 0° and 10°... $w = \mp 0·17$ }

TABLE III.—Indices of Refraction of Water for the Thallium-line.

Temperature (R.)		Refracting angle.	Angle of least deviation.			Index of refraction.		Difference.	
Read.	Corrected.		φ.	ψ.	δ.	Observed.	Calculated.	Δ.	Δ².
0	0	58 38 31	22 5 7	58 18	23 3 25	1·33566	1·33568	−0·2	0·04
0	0·	58 38 31	22 5 10	58 18	23 3 28	1·33568	1·33568	0	0·00
1·8	1·8	58 38 31	22 5 0	58 18	23 3 27	1·33567	1·33567	0	0·00
2·7	2·8	58 38 31	22 5 0	58 18	23 3 18	1·33565	1·33566	−0·1	0·01
3·4	3·5	58 38 31	22 5 0	58 18	23 3 18	1·33564	1·33564	0	0·00
4·0	4·1	58 38 31	22 4 55	58 17	23 3 12	1·33562	1·33563	−0·1	0·01
8·0	8·2	58 38 31	22 4 4	58 15	23 2 19	1·33542	1·33546	−0·4	0·16
9·8	10·0	58 38 2	22 3 45	58 16	23 2 1	1·33540	1·33535	+0·5	0·25
15·8	16·3	58 38 19	22 1 16	58 8	22 59 24	1·3348	1·3348	0	0·00
18·1	18·7	58 38 19	21 59 52	58 1	22 57 57	1·3345	1·3345	−0·5	0·25
20·9	21·6	58 38 19	21 58 27	57 48	22 56 28	1·341	1·341	0	0·00
28·0	29·0	58 38 3	21 53 17	57 34	22 51 5	1·3329	1·3330	−1	1·00
36·0	36·9	58 38 3	21 47 10	57 33	22 44 44	1·3316	1·3315	+1	1·00
36·1	37·0	58 38 3	21 46 50	57 10	22 44 23	1·3314	1·3315	−1	1·00
45·8	46·9	58 38 3	21 37 25	56 58	22 34 35	1·3291	1·3292	−1	1·00
49·1	50·2	58 38 3	21 33 30	56 51	22 30 28	1·3283	1·3284	−1	1·00
52·0	53·3	58 38 23	21 30 40	56 45	22 27 32	1·3276	1·3276	0	0·00
55·1	56·6	58 38 8	21 27 58	56 26	22 24 43	1·3270	1·3267	+3	9·00
61·0	62·5	58 38 8	21 20 20	56 23	22 16 46	1·3252	1·3252	0	0·00
61·7	63·3	58 38 12	21 19 15	56 6	22 15 38	1·32495	1·32495	0	0·00
68·0	69·6	58 38 12	21 12 22	56 0	22 8 28	1·3233	1·3231	+2	4·00
69·1	71·7	58 37 55	21 11 20	55 57	22 7 23	1·3231	1·3228	+3	9·00
70·6	72·2	58 37 55	21 8 40	55 58	22 4 37	1·32255	1·3227	−1·5	2·25
70·7	72·4	58 38 12	21 9 0	55 52	22 2 58	1·32254	1·3226	−0·6	0·36
72·4	74·2	58 38 12	21 6 45	55 52	22 2 37	1·3220	1·3222	−2	4·00
									ΣΔ² = 34·33

In order to correct for the excentricity of the prism, the above-mentioned distances had to be measured.   For the first arrangement, to which belong the observations marked with an asterisk,—

<div align="right">millims.</div>

(1) Distance of the slit from the axis of $\left\{\begin{array}{l} 7795 \\ 7796 \\ 7793 \end{array}\right.$
    rotation of the universal circle

<div align="center">Mean   .   .   . $=\overline{7795}$</div>

(2) Distance of the prism from the uni- $\left\{\begin{array}{l} 342\cdot2 \\ 342\cdot1 \\ 341\cdot7 \end{array}\right.$
    versal circle   .   .   .   .   .   .

<div align="center">Mean   .   .   . $=342\cdot0$</div>

In the second arrangement there was found—

Corresponding with (1).	Corresponding with (2).
7789	337·4
7791	337·5
7790	337·3
7790·5	337·4
7790	337·2
7790	337·1

Mean . $=7790\cdot1$ Mean . $=337\cdot3$

From the complete agreement between the results obtained from both arrangements we can conclude as to the accuracy of the method.

The centres of the direct and of the refracted image of the slit did not lie in a horizontal plane, but differed $7'\ 45''$ in height. The correction to be introduced is easily got from the right-angled spherical triangle A B B', fig. 9.   Let A B' be the deviation of the luminous ray read off on the chief circle, and B B' the difference of height; then the angle of deviation which has really to be measured is A B, and $\cos A B = \cos A B' - \cos B B'$. If we further notice that $\log \cos B' = 9\cdot9999988$, it is evident that no correction need be made of the angle read off.

The angle of least deviation, read directly off on the universal circle, had, on account of the excentricity of the prism, to receive a $+$ correction ψ.   To facilitate this, small auxiliary Tables were constructed giving corrections for every five minutes.

Finally, concerning the errors of individual observations, they may arise from want of accuracy (1) in the determination of ϕ

and α, (2) in the determination of the distances, (3) in the determination of the temperature.

The measurement of the least deviation may be considered correct to $5''$ between the temperatures $0°$ and $10°$, where there is no difficulty attending the maintenance of the temperature constant. With higher temperatures the errors may easily increase to $30''$; and for the highest temperatures, with the thallium and lithium-lines, which were then rather dull, the errors, judged from the results, rise to $1'$. Hence, for the lower temperatures, we may rely upon accuracy as far as three units in the fifth decimal place. From $10°$ to the higher temperatures the fourth decimal place may be subject to an error of one unit. Between $70°$ and $80°$ the error may rise as far as two units of the fourth decimal place, since an error in ϕ of $1'$ exactly corresponds to two units of the fourth decimal place in the index.

The determination of the lengths may also give rise to errors, since the magnitude of the correction ψ depends upon them. An alteration in the greater distance of 10 millims. corresponds to an alteration of $5'$ in ψ. This error, however, cannot exceed 4 millims. The separate measurements of this value agree with one another much more perfectly (see p. 342). An alteration of 10 millims. in the shorter distance corresponds to an alteration of $1' 45''$ in ψ; but I believe, in my method of determination, the error in this length scarcely reaches 2 millims. Errors in the measurement of length may therefore produce alterations in ϕ to the extent of $26''$ in addition to other errors. The probable error in the angular determination of the prism does not exceed $10''$, as was shown by the agreement of the angles measured for a known temperature. These measurements were the more exact because usually these angular measurements were conjoined for the determination of one of the values given. A deviation of $10''$ in α causes a possible error of two units in the fifth decimal place of the index of refraction. The errors in the reading or in the correction of the temperature may reach $0°\cdot3$, which has an almost imperceptible effect for low temperatures, while for higher temperatures it may cause an error of one or two units in the fourth decimal place.

V. *Correlation of the Results.*

After the observations in Tables I., II., III. had been obtained in the manner described, they were first represented graphically in order to see if any of them were so far removed from regular law as to point to some gross error of calculation or observation. As this nowhere appeared, and as the application of tests showed the correctness of the calculation, I endeavoured to express the

evidently regular system of values by means of a mathematical formula.

The idea which immediately suggested itself was to try whether a formula similar to the one usually employed for the coefficients of expansion did not satisfy the experiments. In order to try the fitness of different curves corresponding to these values, some of the observations for the sodium-line were taken, from which four so-called standard values (*Normalorte*) were chosen.

t.	0°.	10°.	40°.	70°.
n_t	1·33380	1·33340	1·32910	1·32115

By the help of these the values of the constants were approximately reckoned. It seemed possible to assume, without in any way departing from the truth, that a formula suitable for the index of refraction for D would be applicable as far as concerned its form to the other two rays. For a curve of the form

$$n_t = a + bt + ct^2$$

we get

$$n_t = 1·3338 - 1·0000332\,t - 0·000002107\,t^2 \quad . \quad (1)$$

from the standard values 0°, 40°, 70°.

This line gives all the first values too small, agrees pretty well at mean temperatures, and diverges rather considerably from the last found values.

$$n_t = 1·3338 - 0·00001099\,t - 0·000002980\,t^2 \left.\vphantom{\begin{array}{c}1\\1\end{array}}\right\} \quad . \quad (2)$$
$$+ 0·000000007936\,t^3. \quad . \quad . \quad . $$

This equation certainly agrees remarkably well with the observations. On comparing the first terms, it is seen that the lineal term is very small compared with the others; and I therefore tried whether any great difference would be made by neglecting it*. The calculation was therefore repeated for

$$n_t = a + ct^2 + dt^3,$$

* It appears, under correction, to the translator that the author's reasoning is here unsound. Calling the terms

1·3338,	0·00001099t,	0·000002980t^2,	0·00000000936t^3

respectively

A,	B,	C,	D,

from $t=$	0	to $t=$	3·7, the terms are in the order of magnitude ABCD,
„	$t=$ 3·7	to $t=$ 37	„ „ „ ACDB,
„	$t=$ 37	to $t=$ 375	„ „ „ ACDB,
„	$t=$ 375	to temperature beyond the thermometric range	ADCB.

Since up to 37° B > D, it is not clear why the linear term should be rejected rather than the cubic one.—F. G.

and it was found that

$$n_t = 1\cdot3338 - 0\cdot000003412\,t^2 + 0\cdot00000001186\,t^3, \quad . \quad (3)$$

a formula which agreed with the observations quite as accurately as the preceding one. An isolated previous observation, however, made it appear probable that for water below 0° the refractive index again diminishes. Bearing this in mind, I imagined that the formula had a symmetrical form, and I finally tried

$$\mu = a + bt^2 + ct^4,$$

and calculated

$$n_t = 1\cdot3338 - 0\cdot000003110\,t^2 + 0\cdot0000000001078\,t^4. \quad . \quad (4)$$

This formula agrees so well with the observations and is so simple that I determined to adopt it *arbitrarily* as the one expressing the alteration in the refractive index, and according to which the arrangement was to be attempted.

Since in $n_t = a + bt^2 + ct^4$ for low temperatures c has only a trifling influence, the indices for 0° were determined from observations between 0° and 10° according to the formula $n = a + bt°$. These values, moreover, are more correct than the other ones, because, in the first place, the temperature of the liquid is only a little different from that of the surrounding air, and therefore the determinations of temperature are more correct, and, secondly, because, in consequence of this, the refracted images of the lines are much more sharp and distinct, whereby the error of adjustment is less.

In this way, by means of the method of least squares,

$$\text{For Li} \quad . \quad . \quad n_0 = 1\cdot33154,$$
$$\text{,, Na} \quad . \quad . \quad n_0 = 1\cdot33374,$$
$$\text{,, Th} \quad . \quad . \quad n_0 = 1\cdot33568.$$

These values were controlled by the method of least squares according to the formula

$$n_t - a = bt^2 + ct^4,$$

or

$$m = bt^2 + ct^4.$$

Since now both m and t are affected by error, we do not find

$$m - bt^2 - ct^4 = 0,$$

but

$$m - bt^2 - ct^4 = \delta.$$

But $\Sigma\delta^2$ should be a minimum, *i. e.*

$$\frac{\partial\Sigma\delta^2}{\partial b}=0 \text{ and } \frac{\partial\Sigma\delta^2}{\partial c}=0;$$

from these two differential equations we get

$$\Sigma mt^2=b\Sigma t^4+c\Sigma t^6 \text{ and } \Sigma mt^4=b\Sigma t^6+c\Sigma t^8,$$

and hence

$$b=\frac{\Sigma mt^2\Sigma t^8-\Sigma mt^4\Sigma t^6}{\Sigma t^4\Sigma t^8-(\Sigma t^6)^2}, \quad c=-\frac{\Sigma mt^2\Sigma t^2-\Sigma mt^4\Sigma t^4}{\Sigma t^4\Sigma t^8-(\Sigma t^6)^2}.$$

Accordingly the following formulæ were found for the alteration of the index of refraction of water with the temperature :—

(1) For the lithium-line,

$$n=1\!\cdot\!33154-0\!\cdot\!000003072t^2+0\!\cdot\!0000000001123\,t^4.$$

(2) For the sodium-line,

$$n_t=1\!\cdot\!33374-0\!\cdot\!000003147\,t^2+0\!\cdot\!0000000001205\,t^4.$$

(3) For the thallium-line,

$$n_t=1\!\cdot\!33568-0\!\cdot\!000003267\,t^2+0\!\cdot\!0000000001476\,t^4.$$

The agreement of these formulæ with the observed values, which can be seen in Tables I., II., III., and which may easily be judged of from the graphic representation (Plate V.), may be considered completely satisfactory. For it is only in the highest temperatures, in observations of the lithium- and thallium-lines, that divergences of three units in the fourth decimal place occur, one in each; and these may be fairly attributed to errors of observation.

Further, a Table has been formed from the three formulæ containing the indices of refraction for our three spectral lines for every 2°.

TABLE IV.—Indices of Refraction of Water.

R.	Lithium-line.	Difference.	Sodium-line.	Difference.	Thallium-line.	Difference.
0	1·33154	1	1·33374	1	1·33568	1
2	1·33153	4	1·33373	4	1·33567	4
4	1·33149	6	1·32369	6	1·33563	7
6	1·33143	9	1·33363	9	1·33556	9
8	1·33134	11	1·33354	12	1·33547	12
10	1·33123	13	1·33342	14	1·33535	13
12	1·33110	16	1·33328	16	1·33522	17
14	1·33094	19	1·33312	18	1·33505	20
16	1·33075	20	1·33294	21	1·33485	22
18	1·33055	22	1·33273	23	1·33463	24
20	1·33033	25	1·33250	25	1·33439	27
22	1·33008	27	1·33225	28	1·33412	29
24	1·32981	30	1·33197	31	1·33383	31
26	1·32951	32	1·33166	32	1·33352	33
28	1·32919	33	1·33134	33	1·33319	35
30	1·32886	35	1·33101	36	1·33284	38
32	1·32851	35	1·33065	39	1·33246	39
34	1·32816	40	1·33026	40	1·33207	40
36	1·32776	43	1·32986	42	1·33167	42
38	1·32733	43	1·32944	43	1·33125	44
40	1·32690	44	1·32901	45	1·33081	45
42	1·32646	46	1·32856	46	1·33036	46
44	1·32600	47	1·32810	48	1·32990	48
46	1·32553	48	1·32762	49	1·32942	51
48	1·32505	49	1·32713	51	1·32891	50
50	1·32456	51	1·32662	51	1·32841	50
52	1·32405	52	1·32611	53	1·32791	51
54	1·32353	53	1·32558	53	1·32740	53
56	1·32300	53	1·32505	54	1·32687	53
58	1·32247	53	1·32451	54	1·32634	53
60	4·32194	53	1·32397	55	1·32581	53
62	1·32139	55	1·32342	55	1·32528	52
64	1·32084	55	1·32287	55	1·32476	52
66	1·32029	55	1·32232	55	1·32424	52
68	1·31974	55	1·32177	56	1·32372	50
70	1·31919	55	1·32121	55	1·32322	52
72	1·31864	55	1·32066	54	1·32270	50
74	1·31809	54	1·32012	54	1·32220	49
76	1·31755	54	1·31958	53	1·32171	44
78	1·31701	54	1·31905	52	1·32127	44
80	1·31647		1·31853		1·32083	

We must here remember that the above Table contains the indices of refraction out of water into air of 7° and about 335''' pressure. The relative indices must therefore be reduced to refraction into vacuum (*freier Aether*). According to Biot-Arago's law, the refractive power (*brechende Kraft*) of the air (that is, the square of the refractive index diminished by unity) is proportional to the density. Accordingly for air,

$$n_1{}^2 - 1 = \frac{\text{const. } b \text{ millim.}}{(1 + \alpha t)\ 760 \text{ millims.}}$$

(α, the coefficient of expansion for air, being 0·00367). Now for $t = 0°$ and $b = 760$ millims., according to the same physicists, $n_1 = 0·000294$ is the index of refraction of air, whence the constant is found $= 0·000588$. If now n_1 be the absolute index of refraction for air for $t°$ and b millim. pressure, and n be the relative index of refraction of a medium in air of $t°$ and b millim. pressure, then the absolute index of refraction N is

$$N = n_1 n = n \sqrt{\frac{1 + 0·000588 b}{(1 + \alpha t) 760}}.$$

We might imagine that the temperature of the layers of air next to the prism would be t. A simple calculation shows that it is only necessary to take into account the temperature of the place where the observations are performed, under the hypothesis that the prism is so distant from the object-glass of the telescope that the latter has the temperature of the whole room.

We may suppose that the glass plates have a temperature t, which is the same as that of the liquid, and that the temperature of the air remains constant through each of the narrow layers parallel to the glass plate, but that the temperatures of the succeeding layers diminish as they recede from the prism, until at a certain distance from the prism their temperature is equal to T, that of the surrounding air. I imagine the air to be divided into such thin layers, parallel to the surface of the prism, that the temperature of these layers may be considered constant. In the layer lying next to the glass let the temperature be $t - \epsilon_1 t$, in the following one $t - \epsilon_2 t$, until at last at some distance $t - \epsilon_k t = T$. If a ray of light comes out of a liquid and falls at an angle i upon the closing glass plate, it is broken towards the normal at an angle r (fig. 10). Let N be the absolute index of refraction for water at $t°$, and n that of glass at $t°$; let ν_1, ν_2, ν_3 be the absolute indices of the refraction of air for the temperatures $t + \epsilon_1 t$, $t + \epsilon_2 t$, &c., and ν_k that for T°. The relative indices of refraction, through which the relation of the angle of refraction to the angle of incidence is determined, are the quotients of the absolute indices out of the one into the other medium. Consequently r and i depend upon one another according to the equation

$$\sin r = \frac{n}{N} \sin i.$$

Since the bounding surfaces of the air-layers are always assumed to be parallel to the parallel surfaces of the glass plates, the angles of refraction out of a preceding medium are the incident angles into the succeeding one; and consequently, in our equation,

$$\sin r_1 = \frac{\nu_1}{n}\sin r, \quad \sin r_2 = \frac{\nu_2}{\nu_1}\sin r_1, \ \&\mathrm{c.},$$

$$\sin r_k = \frac{\nu_k}{\nu_{k-1}}\sin r_{k-1}.$$

If each of these equations be substituted in succession in the following one, we find that

$$\sin r_k = \frac{\nu_k}{\mathrm{N}}\sin i;$$

that is, the refraction out of a warmed hollow prism into air of T° is just the same as if the ray had passed out of the warmed liquid into air of the temperature of the place of observation, and had only suffered a lateral parallel displacement.

The atmospheric pressure during the observation varied between 337''' and 330''' (Paris lines), for which we may put the mean value reduced to millimetres*, 755 millims. By means of the formula given on page 348 the relative indices of refraction may be reduced to absolute ones. The correction is

+0·00038	for index of refraction		1·33570
+0·00038	,,	,,	1·32710
+0·00038	,,	,,	1·31850

Consequently we have only to add 0·00038 to all the values contained in Table IV. in order to obtain thence the absolute indices of refraction of water for the lithium-, sodium-, and thallium-lines.

From the numerical values found in Table IV. we get the following results.

(1) The refractive index of water decreases continuously, and therefore the velocity of propagation of light increases continuously, from 0° to 80° R., without showing any variation from the law of change at the maximum density. The change of the index of refraction with the temperature may be satisfactorily expressed by means of a formula,

$$\mu = a - bt^2 + ct^4.$$

At higher temperatures, for the lithium-line at 77° R., for the sodium-line at 70° R., and for the thallium-line at 61° R., there are points of contrariflexure. These may be introduced by the nature of the formula, and are not necessarily based upon the actual nature of the phenomena. The diminution of the index

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* A difference of 10''' in atmospheric pressure introduces a difference of not quite one unit in the fifth decimal place, in the calculation of the absolute index of refraction; so that the above introduction of a constant pressure is allowable.

of refraction for each $1°$ R. increases from $0·00005$ to $0·00028$, and is greatest at the highest temperatures.

(2) The relative dispersion between the sodium and lithium-lines is expressed by

$$D_1 = n_{\mathrm{Na}} - n_{\mathrm{Li}} = 0·00220 - 0·0000000751\, t^2 \left.\right\} \quad . \quad . \quad (4)$$
$$+ 0·0000000000082 t^4, \quad . \quad . \quad . \quad$$

and attains a minimum when $\dfrac{dD_1}{dt} = 0$, *i. e.* at $67°·6$ R.

The relative dispersion between sodium and thallium is expressed by

$$D_2 = n_{\mathrm{Th}} - n_{\mathrm{Na}} = 0·000194 - 0·000000120 t^2 \left.\right\} \quad . \quad (5)$$
$$+ 0·0000000000271 t^4, \quad . \quad . \quad .$$

and becomes a minimum when $\dfrac{dD_2}{dt} = 0$, *i. e.* at $47°·1$ R.

The relative dispersion between the lithium- and thallium-lines,

$$D_3 = 0·00414 - 0·000000195\, t^2 + 0·0000000000353 t^4, \quad (6)$$

is least (between $0°$ and $80°$ R.) at $52°·6$ R. These last results relating to the dispersion in water may certainly cause surprise, since they are partly in contradiction to Gladstone and Dale's results. The values, however, here concerned are very small; and the small difference in undular length between the rays chosen by us is not calculated to decide conclusively whether we have to do with the results of an interpolation-formula which does not quite suit, or really with a natural phenomenon.

By the help of these formulæ for the indices of refraction we are in a position to state the three relations,

$$a_1 + b_1 t^2 + c_1 t^4 = A + \frac{B}{\lambda_1^2} + \frac{C}{\lambda_1^4},$$

$$a_2 + b_2 t^2 + c_2 t^4 = A + \frac{B}{\lambda_2^2} + \frac{C}{\lambda_2^4},$$

$$a_3 + b_3 t^2 + c_3 t^4 = A + \frac{B}{\lambda_3^2} + \frac{C}{\lambda_3^4},$$

from which A, B, and C may be derived as functions of the temperature.

As water shows very little dispersion, we may, in Cauchy's dispersion-formula

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \cdots,$$

put $n = A + \dfrac{B}{\lambda^2}$ without much error for the first approximation.

We shall therefore be satisfied with determining A and B for a subsequent purpose from the formulæ for the lithium-ray (1) and for the thallium-ray (3).

We find

$$A_t = \alpha_1 - \alpha_2 t^2 + \alpha_3 t^4,$$

whence

$$\alpha_1 = 1\cdot32432$$
$$\log \alpha_2 = 0\cdot436957 - 6,$$
$$\log \alpha_3 = 0\cdot709100 - 11 ;$$

$$B_t = \beta_1 - \beta_2 t^3 + \beta_3 t^4,$$

whence

$$\log \beta^1 = 0\cdot511831 - 9,$$
$$\log \beta^2 = 0\cdot184866 - 13,$$
$$\beta^3 = 0\cdot442606 - 17.$$

Making use of the formula

$$n_{t,\lambda} = A_t + \frac{B}{\lambda}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

and inserting the corresponding values of λ and t, we may find, exactly to units of the fourth decimal place, the index of refraction for every Fraunhofer's line we please and for every temperature (between $0°$ and $80°$ R).

In order to show that the dispersion-formula (7) is nearly sufficient to give the relations of refraction for all temperatures, I adduce here some values of the D line calculated by its means, and place side by side with them the numbers taken directly out of the Table.

Index of Refraction for the D line.

R.	Reckoned from (7).	Observed and compared.	Difference.
0	1·33369	1·33374	−0·5
8	1·3334	1·3335	−1
16	1·3329	1·3329	0
24	1·3319	1·3320	−1
32	1·3306	1·3306	0
40	1·3290	1·3290	0
48	1·3271	1·3271	0
56	1·3250	1·3250	0
64	1·3229	1·3229	0
72	1·3207	1·3207	0
80	1·3187	1·3185	+2

As Cauchy's first approximation gives satisfactory results, and the calculation of the coefficients in Christoffel's otherwise far

preferable dispersion-formula is troublesome*, I consider this formula (7) to be sufficient ; and I believe I have by its means sufficiently determined the alteration caused by heat in the velocity of the propagation of light in water.

VI. *On the relation between the Velocity of the Propagation of Light and the Density.*

It is well known that the theory of emission has given the following relation between the velocity of propagation of light and the density[†],

$$\frac{n^2 - 1}{d} = \frac{4k}{v^2},$$

where v denotes the velocity of light in air, and k is a constant. Hence the so-called refractive power (*brechende Kraft*) $n^2 - 1$, divided by the density, would be a constant quantity. It remained necessarily impossible to discover a relation between the optical conditions and the density of bodies as long as, in employing the vibration hypothesis, the mathematical theory, in establishing the differential equations of the motion of the æther, neglected the existence of material molecules and their action upon the æther molecules. But an analytical solution of this problem may be safely predicted now that it is almost universally admitted with Cauchy[‡], Redtenbacher[§], Lorenz[||], and Briot[¶], that in consequence of an attraction between the material molecules and the æther molecules, and a reciprocal repulsive action between the æther molecules, there is in substances a periodical arrangement of the æther molecules around the material ones. A more exact discussion of the number of material

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* Christoffel, *Berichte der Berliner Akademie für* 1861, vol. ii. pp. 906–919 & 997–999.
    This formula, based certainly upon the insufficient foundation of Cauchy's "Mémoire sur la Dispersion," is quite as useful as Cauchy's formula as an empirical expression, and allows a very interesting indication of the constants n_2 and λ_0. It is

$$n = \frac{n_0 \sqrt{2}}{\sqrt{1 + \dfrac{\lambda_0}{\lambda}} + \sqrt{1 - \dfrac{\lambda_0}{\lambda}}},$$

where n is the index of refraction, λ the undular length, and n_0 and λ_0 two constants dependent upon the nature of the medium.
    † Laplace, *Mécanique Céleste*, vol. iv. book 10. p. 264.
    ‡ " Mémoire sur les vibrations d'un double système de molécules, et de l'éther contenu dans un corps cristallisé," *Mémoires de l'Académie*, vol. xxiv. pp. 599–614 &c.
    § *Dynamidensystem*, pp. 11–28.
    || " Ueber die Theorie des Lichts," Pogg. *Ann.* vol. cxxi. p. 579.
    ¶ *Essais sur la théorie mathématique de la lumière.*

molecules which finally act upon a given æther molecule, a number which must appear in the coefficients of the differential equations of the motion, must lead to a relation between the velocity of luminous propagation and the density of bodies. The fundamental conception is certainly at present wanting concerning the method to be adopted. But not only the possibility, but also the necessity of a connexion appears from the nature of the differential equations supported by the views we have given. It may be permitted here to return to a point already touched upon. On page 265 we arrived at the surprising result that the velocity of propagation of light in liquids and gases increases universally with the increase of their temperature, while with most solid bodies it diminishes. Such an opposite behaviour may be explained by assuming that there occurs in æther, on heating it, an increase of density or a diminution of elasticity. The enormous alteration in density of liquids and gases, brought about by their increase of volume, causes such a diminution in the density of the circumposed æther, as entirely to mask the alteration specific to the æther itself, because the material molecules in their separation from one another are accompanied by the enveloping æther. But the variation in the density of solid bodies being small, their influence upon the æther may be so completely overbalanced by the increase of density or diminution of elasticity which the æther undergoes with increase of temperature, that an increase of the index of refraction is brought about. We thus see that these phenomena are not inexplicable. And although the hypothesis adopted for their explanation is at present only brought forward to explain facts, it is nevertheless simple and acceptable. We see, however, that here also the alteration in the density of a body is in uninterrupted connexion with the optical relations.

The opinion of Jamin, that the vibration hypothesis does not require any such definite connexion, must be rejected as unfounded, since, although hitherto no such relation has been established from theory, while the necessity for the existence of one has been felt, although vaguely, by most physicists, attempts have been made to establish divers empirical relations which have not, however, as yet proved satisfactory. These were, for the most part, obtained accidentally and without any substantial foundation. It was tried whether any function of the index of refraction, or of Cauchy's constants A and B, gave a plausible relation to the density.

For a long time after the undulatory theory had gained support, it was still supposed that the refractive power $n^2 - 1$ was a constant. This view was caused by the proof given by Biot and Arago of its constancy for gases, and by the extension of the

proof to gaseous mixtures. This error found further support from the fact that the constant $\dfrac{n^2-1}{d} = $ const. might be used, as Beer and Kremers[*] showed, to calculate the indices of refraction for saline solutions from their constituents. In the same way, Hoek[†], assuming this relation, repeated the calculations for Deville's experiments on the refractive indices of liquid mixtures, and obtained perfectly concordant results. Forthomme[‡] also adopted the refractive power (*brechende Kraft*) as basis for similar investigations. Schrauf[§] published a very elaborate criticism against the constancy of the quotient between the refractive power and density, for which he proposed a new relation, which he strove to support by numerical values. He proceeds from Cauchy's formula of dispersion, and makes use of the first approximation,

$$\mu = A + \frac{B}{\lambda^2}.$$

In rather an arbitrary manner, the foundation of which I am not alone in being unable to understand, Schrauf arrived for A at the differential equation

$$A \cdot dA = M \cdot dD, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(I.)}$$

where M represents a constant and D the density of the body.

Schrauf gives the derivation of another equation in some such terms as the following[||].

The coefficient of dispersion depends, according to Cauchy, upon a quadratic; the dispersion can only be caused by disturbances of a higher order; and so, as is shown by comparison of the differences, we may rightly assume that the alteration in B is a function both of the density and its alterations, and that accordingly

$$dB = ND \cdot dD, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \text{(II.)}$$

where N represents a new constant.

Since the confirmation of these differential equations for other reasons is not apparent, they are only valid provided the laws derived from them are really confirmed by experience. For the inferior limit of integration we make use of the relation that for $D = 0$ there is no refraction and no dispersion, and that accord-

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[*] Pogg. *Ann.* vol. ci. p. 133.   [†] Ibid. vol. cxii. p. 347.
[‡] *Ann. de Chim. et de Phys.* vol. lv. p. 307.
[§] " Ueber die Abhängigkeit der Fortpflanzungsgeschwindigkeit des Lichtes von der Körperdichte," Pogg. *Ann.* vol. cxvi. pp. 193–249.
[||] Pogg. *Ann.* vol. cxvi. p. 204.

ingly A=1 and B=0. Then from (I.) and (II.) we get

$$\frac{A^2-1}{D} = M, \quad \ldots \quad \ldots \quad (III.)$$

$$\frac{B}{D^2} = N. \quad \ldots \quad \ldots \quad \ldots \quad (IV.)$$

Schrauf calls M the "specific refractive power" (*specifisches Brechungsvermögen*), and he calls N the "specific dispersive power" (*specifisches Dispersionsvermögen*).

Although Schrauf's views concerning the cause of dispersion and the effect of the material molecules on light contain much truth, and the consistent carrying out of his hypothesis must be called very able, it is impossible to refrain from applying the term obscure, if not confused, to the commencement of his work.

In order to establish the constancy of the magnitude M and N, he takes the experiments of Gladstone and Dale (1858), and uses also whatever other materials are at his disposal, such as the observations of Deville, Cahours, Handl and Weiss, De Roux, and others.

It appeared that $\frac{A^2-1}{D}$ was approximately constant, but diminished continually as the temperature increased. The constancy of B does not appear to me to be even approximately proved by the numerical data. Schrauf endeavoured to account for the diminution of the magnitude M by assuming that the angle of the prism had changed by increase of temperature—a supposition which Gladstone and Dale[*] have rejected as totally unfounded.

All the elegant subsequent deductions, founded upon the fundamental assumption that M and N are independent of the temperature, fall to the ground as soon as it is shown that these magnitudes are not constant, but vary considerably with the temperature. We cannot, therefore, regard it proved in this manner that the refractive power is constant, or a multiple of the simplest factors of the series of natural numbers,

$$\frac{n(A^2-1)}{d} = B,$$

nor, further, that only the variations of density and not the elasticity is of considerable influence upon the velocity of propagation of light, nor that the latter is only a function of the density, &c.

[*] Phil. Trans. 1863, p. 343.

Also the conclusions drawn in later treatises of Schrauf, "On the Influence of the Chemical Conditions on the Velocity of Propagation of Light"[*], and also " On the Determination of the Refractive Equivalents of the Elements"[†], are rendered invalid by the proof that *neither* M *nor* N *are constants,* but that M only may be considered so in rather rough approximation. Two schemes, which are given on pages 357 and 359, give numerical values for M and N for certain substances. The first of these is taken, for the most part, out of the second treatise by Gladstone and Dale[‡]; the second I have calculated from my own observations for water.

In the treatise mentioned, Gladstone and Dale suppose there to be another relation between A and D, namely $\dfrac{A-1}{D} = \text{const.}$, or $\dfrac{n_H - 1}{D} = \text{const.}$, while they entirely set aside the constancy of $\dfrac{B^2}{D}$. In regard to Schrauf's magnitude M, they say, " The 'absolute refractive power' is evidently not a constant," and prove their assertion by numbers. For the calculation of A they employed their own observations, while for the density they used the numbers which Kopp gave in his " Investigations on Specific Gravity and Expansion by Heat, and on the Boiling-Point of some Liquids"[§]. The employment for one and the same calculation of constants derived from two different kinds of the same liquid cannot be considered trustworthy, because the different degree of chemical purity may give rise to considerable differences. At all events, such great differences in density as are given in the works of Pierre[||], Kopp[¶], and Matthiessen[**] are to be attributed chiefly to the different degrees of purity in the preparations.

I am quite conscious that I am also so far open to the same reproach, as I have made no determination of the expansion of the water used by me. I have only been prevented from carrying out this experiment by want of time. My apparatus for this purpose is already made; the constants are determined, and the data for water will be adduced in the publication of the continuation of my memoir. I believe that the numbers obtained by others may be more safely used in the case of water than in that

[*] Pogg. *Ann.* vol. cxix. pp. 461–480, and pp. 553–572.
[†] Ibid. vol. cxxvii. p. 175.
[‡] " Researches on the Refraction, Dispersion, and Sensitiveness of Liquids," Phil. Trans. vol. cliii. (1863), pp. 307–343.
[§] Pogg. *Ann.* vol. lxxii. p. 42.
[||] *Ann. de Chim. et de Phys.* 1825, Nov. and Dec. p. 325.
[¶] Pogg. *Ann.* vol. lxxii. p. 42.
[**] Pogg. *Ann.* vol. cxxviii. pp. 512–540. Report of British Association, 1863, p. 37.

of other bodies, because it may, within narrow limits, be obtained almost chemically pure. Moreover Kremers* and Matthiessen† have proved that small mixtures of salts do not appreciably alter the constants of expansion of water.

In my experiments I used distilled water out of Professor Kolbe's chemical laboratory, and I distilled it frequently myself with every care. For every separate determination, moreover, the absorbed air was expelled by continual boiling.

We may here introduce a scheme showing some numerical values for the relation given between the velocity of propagation of light and the density.

A signifies the constant term in Cauchy's dispersion-formula, D is the density, n_H is the index of refraction for Fraunhofer's line H. (See Gladstone and Dale, Phil. Trans. vol. cliii. pp. 321 & 322.)

Substance.	Temp.	Volume.	A.	$\dfrac{A-1}{D}$.	$\dfrac{n_H-1}{D}$.	$\dfrac{A^2-1}{D}$.	Differ- ence.
Sulphide of carbon {	11°	0·9554	1·5960	0·5694	0·5930	1·4782	
	22·5	0·9685	1·5865	0·5680	0·5923	1·4714	−68
	36·5	0·9854	1·5753	0·5668	0·5916	1·4599	−15
Extreme difference...	25·5	+0·0300	−0·0207	−0·0025	−0·0014	−0·0183	
Water ....{	1	0·9999	1·3227	0·3227	0·3300	0·7495	+ 2
	15·5	1·0007	1·3228	0·3230	0·3300	0·7497	− 5
	27·5	1·0034	1·3216	0·3227	0·3300	0·7492	− 6
	48·0	1·0109	1·3193	0·3227	0·3295	0·7486	
Extreme difference...	47	+0·0110	−0·0035	−0·0003	−0·0005	−0·0009	
Alcohol ....{	0	0·9132	1·3598	0·3286	0·3480	0·7754	−38
	20	0·9326	1·3518	0·2518	0·3478	0·7716	−41
	40	0·9324	1·3435	0·0435	0·3173	0·7675	−47
	60	0·9762	1·3347	0·3347	0·3473	0·7628	
Extreme difference...	40	+0·0630	−0·0251	−0·0014	−0·0007	−0·0126	
Formiate of ethyle, { $C^4 H^5 HO^3, O C^2$	22	1·0305	1·3476	0·3582	0·3607	0·8409	−12
	31	1·0436	1·3434	0·3584	0·3611	0·8397	−14
	40	1·0573	1·3390	0·3584	0·3615	0·8389	
Extreme difference...	18	+0·0268	−0·0086	+0·0002	+0·0008	−0·0026	
Benzole ....{	10·5	1·0125	1·4777	0·4836	0·5371	1·1999	−46
	23	1·0228	1·4704	0·4834	0·5370	1·1944	−81
	39	1·0481	1·4601	0·4822	0·5353	1·1863	
Extreme difference...	28·5	+0·0356	−0·0176	−0·0014	−0·0018	−0·0127	

* Pogg. *Ann.* vol. cxiv. p. 41.
† Pogg. *Ann.* vol. cxxviii. pp. 512–540. Report of British Association, 1863, p. 37.

I add here the values of the same constants obtained from my experiments, and employ the latest and most probably the most trustworthy results obtained by Matthiessen on the expansion of water. These numbers were got by weighing, in the liquid to be examined, a solid body whose expansion was exactly known. As all precautions were taken in these experiments, and this method involves fewer constant sources of error than that employed by Kopp (determining by means of an instrument resembling a thermometer—dilatometer), I think I am justified in considering Matthiessen's data the most correct. In order to investigate the influence of the maximum density of water upon the relations under examination, I made use of the numbers given by Kopp between 0° and 8° C., since Matthiessen has not extended his observations to temperatures below 4° C. As the data for the density of water given by different equally eminent physicists differ from one another in the fourth decimal place*, I content myself with giving the results to the fifth decimal place.

Matthiessen gives two formulæ to express the expansion of water between 0° and 100° C.; the one is applied from 4° to 32°, and the other between 32° and 100° C. These formulæ are :—

For $t = 4°$ to $t = 32°$,

$$v_t = 1 - 0.00000253(t-4) + 0.00000389(t-4)^2$$
$$- 0.00000007173(t-4)^3.$$

For $t = 32°$ to $t = 100°$,

$$v_t = 0.999695 + 0.0000054724t^2 - 0.00000001126t^3.$$

Kopp gives for water between 0° and 25° C.,

$$v_t = 1 - 0.000061045t + 0.0000077184t^2 - 0.00000003734t^3.$$

In order to reduce Matthiessen's numbers, which are referred to the volume at 4° C. as unit, to the volume at 0° C. as unit, they must be multiplied by 0.99988.

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* See Matthiessen's collation of the results of various observers, Pogg. *Ann.* vol. cxxviii. p. 534.

Water.

Tempera- ture, C.	volume, $v^0 = 1.$	A.	$B10^{12}.$	$M = (A^2 - 1)v.$	$N = Bv^3 10^{12}.$	$(A-1)v.$
0	1·000000	1·32432	3250	0·75382	3250	0·32432
1	0·999947	1·32432	3250	0·75376	3250	0·32430
2	0·999908	1·32431	3250	0·75372	3249	0·32428
3	0·999885	1·32430	3248	0·75368	3248	0·32426
4	0·999877	1·32429	3247	0·75365	3247	0·32425
5	0·999883	1·32428	3246	0·75362	3246	0·32424
6	0·999903	1·32426	3245	0·75360	3245	0·32423
7	0·999938	1·32424	3245	0·75357	3245	0·32422
8	0·999986	1·32421	3243	0·75352	3243	0·32420
10	1·00015	1·3241	3240	0·7534	3240	0·32415
20	1·00169	1·3236	3213	0·7532	3224	0·32415
30	1·00423	1·3228	3171	0·7529	3198	0·32415
40	1·00761	1·3216	3122	0·7522	3177	0·32405
50	1·01185	1·3201	3076	0·7514	3149	0·32390
60	1·01684	1·3183	3044	0·7503	3148	0·3237
70	1·02253	1·3162	3043	0·7489	3182	0·3233
80	1·02882	1·3140	3088	0·7475	3194	0·3230
90	1·03568	1·3115	3202	0·7457	3435	0·3226
100	1·04303	1·3089	3405	0·7439	3705	0·3222

From the above numbers we see that *the magnitudes* M *and* N *given by Schrauf are by no means constants,* but vary continually with the temperature. If all the differences did not fall on the same side, and if the increase and diminution were not so perfectly regular as they actually are, we might still be in doubt. But since the sign of the differences in the column $\dfrac{A^2-1}{v}$ never alters within the limits of observation, the above assertion can scarcely be other than true.

At the same time it is remarked that the maximum density is not able to overcome the diminution either of $\dfrac{A^2-1}{d}$, or of $\dfrac{A-1}{d}$; both magnitudes continually increase with increasing temperature. Also the "specific refractive power" $\dfrac{A-1}{d}$, which, according to Gladstone and Dale, should be constant, diminishes so regularly with the temperature that there can be no possibility of its constancy. The numbers reckoned for this value from their own experiments by these physicists themselves, show the distinct and well-marked tendency of the value to diminish at higher temperatures.

2 B 2

That $N = \dfrac{B}{d^2}$ is also variable with the temperature, appears distinctly from the second Table, even if the observations above 60° are not taken into account, since small errors in the index of refraction exercise a great influence upon the value of B.

The hitherto advanced empirical relations therefore cannot be maintained, and the so-called "specific refractive force" (*specifische brechende Kraft*) changes with the temperature.

I consider it unnecessary to endeavour to introduce new relations between the velocity of the propagation of light and the density of bodies, since mathematical investigations will certainly soon give the desired solution, and then it will merely remain to compare the theory with experiment.

The proof that Schrauf's "specific force" M (*specifische Kraft*) and his "specific dispersion power" N (*specifisches Dispersionsvermögen*), which has been given by the adduced numbers, are not constants, overthrows all the conclusions grounded upon this assumption, and the further investigations based upon them. The differential equations which he gives are accordingly not justified by experience.

XLII. *On* Mr. Grove's "*Experiment in Magneto-electric Induction.*" *In a Letter to* W. R. Grove, *F.R.S.*[*]

8 Palace Gardens Terrace, W.
March 27, 1868.
Dear Sir,

SINCE our conversation yesterday on your experiment on magneto-electric induction[†], I have considered it mathematically, and now send you the result. I have left out of the question the secondary coil, as the peculiar effect you observed depends essentially on the strength of the current in the primary coil, and the secondary sparks merely indicate a strong alternating primary current. The phenomenon depends on the magneto-electric machine, the electromagnet, and the condenser.

The machine produces in the primary wire an alternating electromagnetic force, which we may compare to a mechanical force alternately pushing and pulling at a body.

The resistance of the primary wire we may compare to the effect of a viscous fluid in which the body is made to move backwards and forwards.

The electromagnetic coil, on account of its self-induction, resists the starting and stopping of the current, just as the mass

[*] Communicated by Mr. W. R. Grove, F.R.S.
[†] See Phil. Mag. S. 4. March 1868, p. 184.

of a large boat resists the efforts of a man trying to move it backwards and forwards.

The condenser resists the accumulation of electricity on its surface, just as a railway-buffer resists the motion of a carriage towards a fixed obstacle.

Now let us suppose a boat floating in a viscous fluid, and kept in its place by buffers fore and aft abutting against fixed obstacles, or by elastic ropes attached to fixed moorings before and behind. If the buffers were away, the mass of the boat would not prevent a man from pulling the boat along with a long-continued pull; but if the man were to push and pull in alternate seconds of time, he would produce very little motion of the boat. The buffers will effectually prevent the man from moving the boat far from its position by a steady pull; but if he pushes and pulls alternately, the period of alternation being not very different from that in which the buffers would cause the boat to vibrate about its position of equilibrium, then the force which acts in each vibration is due, partly to the efforts of the man, but chiefly to the resilience of the buffers, and the man will be able to move the boat much further from its mean position than he would if he had pushed and pulled at the same rate at the same boat perfectly free.

Thus, when an alternating force acts on a massive body, the extent of the displacements may be much greater when the body is attracted towards a position of equilibrium by a force depending on the displacement than when the body is perfectly free.

The electricity in the primary coil when it is closed corresponds to a free body resisted only on account of its motion; and in this case the current produced by an alternating force is small. When the primary coil is interrupted by a condenser, the electricity is resisted with a force proportional to the accumulation, and corresponds to a body whose motion is restrained by a spring; and in this case the motion produced by a force which alternates with sufficient rapidity may be much greater than in the former case. I enclose the mathematical theory of the experiment, and remain,

<div style="text-align:center">

Yours truly,

J. Clerk Maxwell.

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Mathematical Theory of the Experiment.

Let M be the revolving armature of the magneto-electric machine, N, S the poles of the magnets, x the current led through the coil of the electromagnet R, and interrupted by the con-

denser C.   Let the plates of the condenser be connected by the additional conductor *y*.
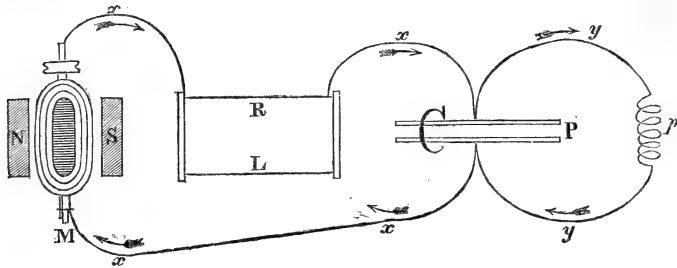
Let M sin θ be the value of the potential of the magnets on the coil of the armature; then if the armature revolves with the angular velocity *n*, the electromotive force due to the machine is M*n* cos *nt*.

Let R be the resistance of the wire which forms the coil of the armature M and that of the fixed electromagnet.

Let L be the coefficient of self-induction, or the " electromagnetic mass " of these two coils taken together.

Let *x* be the value of the current in this wire at any instant, then L*x* will be its " electromagnetic momentum."

Let C be the capacity of the condenser, and P the excess of potential of the upper plate at any instant, then the quantity of electricity on the upper plate is CP.

Let ρ be the resistance of the additional conductor, and *y* the current in it. We shall neglect the self-induction of this current.

We have then for this conductor,

$$P = \rho y. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For the charge of the condenser,

$$C \frac{dP}{dt} = x - y. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For the current *x*,

$$Mn \cos nt + Rx + L \frac{dx}{dt} + P = 0. \quad . \quad . \quad . \quad (3)$$

If we assume

$$x = A \cos (nt + \alpha),$$

we find

$$A^2 = \frac{M^2 n^2 (1 + C^2 \rho^2 n^2)}{\rho^2 \{(1 - LCn^2)^2 + R^2 C^2 n^2\} + 2R\rho + R^2 + Ln^2},$$

$$\alpha = \cot^{-1} \frac{1}{C\rho n} - \cot^{-1} \frac{R + \rho - LC\rho n^2}{RC\rho n + Ln}.$$

The quantity of the alternating current is determined by A; and the value of α only affects the epoch of maximum current. If we make $\rho = 0$, the effect is that of closing the circuit of x, and we find

$$A^2 = \frac{M^2 n^2}{R^2 + L^2 n^2}.$$

This expression shows that the condenser has no effect when the current is closed.

If we make $\rho = \infty$, the effect is that of removing the conductor y, and thus breaking the circuit. In this case

$$A^2 = \frac{M^2 n^2}{R^2 + \left(Ln - \dfrac{1}{Cn}\right)^2}.$$

This expression gives a greater value of A than when the circuit is closed, provided $2CLn^2$ is greater than unity, which may be ensured by increasing the capacity of the condenser, the self-induction of the electromagnetic coil, or the velocity of rotation. If $CLn^2 = 1$, the expression is reduced to

$$A = \frac{Mn}{R}.$$

This is the greatest effect which can be produced with a given velocity, and is the same as if the current in the coil had no " electromagnetic momentum."

If the electromagnet has a secondary coil outside the primary coil so as to form an ordinary induction-coil, the intensity of the secondary current will depend essentially on that of the primary which has just been found. Although the reaction of the secondary current on the primary coil will introduce a greater complication in the mathematical expressions, the remarkable phenomenon described by Mr. Grove does not require us to enter into this calculation, as the secondary sparks observed by him are a mere indication of what takes place in the primary coil.

XLIII. *On Geological Time, and the probable Date of the Glacial and the Upper Miocene Period.* By JAMES CROLL, *of the Geological Survey of Scotland*.*

IT is nearly a century ago since Lagrange's determinations of the superior limits of the excentricity of the planetary orbits were published†. The results at which he arrived were

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* Communicated by the Author.
† Memoirs of the Berlin Academy for 1782.

very nearly the same as those which were afterwards obtained by Leverrier.

Before the beginning of the present century the effects which the excentricity of the earth's orbit may have on climate were discussed. But about thirty-five years ago the question as to how far a change in the amount of excentricity might affect the climate of our globe was considered by Sir John Herschel; and his results were published in the Transactions of the Geological Society of London, vol. iii. (2nd series). But he does not appear at the time to have been aware of the conclusions arrived at by Lagrange regarding the superior limit of the excentricity of the earth's orbit. He came, however, to the conclusion that possibly the climate of our globe may have been affected by variations in the excentricity of its orbit. " An amount of variation," he says, " which we need not hesitate to admit (at least provisionally) as a possible one, may be productive of considerable diversity of climate, and may operate during great periods of time either to mitigate or to exaggerate the difference of winter and summer temperatures, so as to produce alternately in the same latitude of either hemisphere a perpetual spring, or the extreme vicissitudes of a burning summer and a rigorous winter."

Unfortunately, however, this opinion was to a great extent nullified by a statement which afterwards appeared in his ' Treatise on Astronomy,' to which reference will be presently made. Shortly after the appearance of Herschel's paper, the subject was investigated by Arago, Poisson, Humboldt, and other astronomers. The general conclusion arrived at, however, was that the climate of our globe could not be much affected by any change which could take place in the ellipticity of its orbit. The reason which induced astronomers to come to that conclusion seems chiefly to be this : whatever be the extent of the excentricity, the total amount of heat falling on both hemispheres must be the same. The sun, for example, is much nearer the earth when he is over the southern hemisphere than he is when over the northern ; but the southern hemisphere does not on this account receive more heat than the northern ; for, owing to the greater velocity of the earth when nearest the sun, the sun does not remain so long on the southern hemisphere as he does on the northern. These two effects so exactly counterbalance each other that, whatever be the extent of the excentricity, the total amount of heat reaching both hemispheres is the same. And it was considered that this beautiful compensating principle would protect the climate of our globe from being seriously affected by an increase in the excentricity of its orbit,

unless the extent of that increase was very great*. Arago, for example, states that so little is the climate of our globe affected by the excentricity of its orbit, that even were the orbit to become as excentric as that of the planet Pallas (that is, as great as 0·24), "still this would not alter in any appreciable manner the mean thermometrical state of the globe."

This idea, supported by these great authorities, got possession of the public mind ; and ever since it has been almost universally regarded as settled that the great changes of climate indicated by geological phenomena could not have resulted from any change in the relation of the earth to the sun.

There is, however, one effect that was not regarded as compensated. The total amount of heat received by the earth is inversely proportional to the minor axis of its orbit ; and it follows, therefore, that the greater the excentricity, the greater is the total amount of heat received by the earth. On this account it was concluded that an increase of excentricity would tend to a certain extent to produce a warmer climate†.

All those conclusions to which I refer, arrived at by astronomers, are perfectly legitimate so far as the direct effects of excentricity are concerned ; and it was quite natural and, in fact, proper to conclude that there was nothing in the mere increase of excentricity that could produce a glacial epoch. How unnatural and even absurd would it have been to have concluded that an increase in the quantity of heat received from the sun should lower the temperature and cover the country with snow and ice. Neither would excessively cold winters followed by excessively hot summers produce a glacial epoch. If any person had asserted that the purely astronomical causes could produce such an effect, he would certainly and deservedly have been regarded as a fool.

The important fact, however, was overlooked that, although the glacial epoch could not result directly from an increase of excentricity, it might nevertheless do so indirectly. As was stated on a former occasion, the glacial epoch was not due directly to an increase in the excentricity of the earth's orbit, but to a number of physical agents that were brought into operation

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* Herschel in "Treatise of Astronomy," Cabinet Cyclopædia, § 315 ; Outlines of Astronomy, § 368.

Arago in the *Annuaire* for 1834, p. 199. Edinb. New Phil. Journ. for April 1834, p. 224.

Poisson in *Connaissance des Temps* for 1836, pp. 38–54.

Humboldt in *Cosmos*, vol. iv. p. 459. Physical Description of the Heavens, p. 336.

† Herschel in " Discourse on the Study of Natural Philosophy," § 140, Trans. of Geol. Soc. of London, vol. iii. p. 297 (2nd series).

Lyell in ' Principles of Geology,' p. 126, 7th edit.

Professor Haughton in Phil. Mag. for May 1866.

as a result of an increase.   Until those physical circumstances were discovered it was impossible that the true cause of the glacial epoch could be known.   Many of the indirect and physical effects, which in reality were those that brought about the glacial epoch, could not, from the nature of things, have been known previously to recent discoveries in the science of heat.   When the excentricity is about its superior limit, the combined effect of all those causes to which I allude is to lower to a very great extent the temperature of the hemisphere whose winters occur in aphelion, and to raise to nearly as great an extent the temperature of the opposite hemisphere, where winter of course occurs in perihelion.   I have made these remarks in order to obviate certain objections to which I shall afterwards have occasion to refer.

Astronomy and physics not only afford a cause for those abnormal conditions of climate during geological epochs, but they seem to afford also (at least so far as regards very recent epochs) a probable means of arriving at a pretty accurate determination of the date at which those conditions prevailed.

On examining the Tables of excentricity given in former papers* for a million of years back, it will be seen that there are two periods of great duration during which the excentricity continued at a high value.   The one period extended from about 980,000 to about 720,000 years ago, and the other period began about 240,000 years ago and extended down to about 80,000 years ago.   At first I felt disposed to refer the glacial epoch (the time of the true boulder-clay) to the former period; and the latter period, I was inclined to believe, must have corresponded to the time of local glaciers towards the close of the glacial epoch, the evidence of which, in the shape of moraines, is to be found in almost every one of our highland glens.

There was, however, one formidable objection to this view of the matter which presented itself to my mind at the time.   I found, from calculations based on the amount of sediment carried into the Gulf of Mexico by the Mississippi River, that the North American continent is being lowered by subaërial denudation at the rate of $\frac{1}{1388}$ of a foot per annum, and that, consequently, if the rate of denudation be as great in this country as in America, which is by no means improbable, then about 500 feet must have been removed off the face of the country and carried by our rivers into the sea since the period of the boulder-clay, if that period is to be placed 700,000 years back†.   It would therefore follow that the general features of the country must now be totally different from what they were at the close of the

* Phil. Mag. for January 1866 and February 1867.
† Phil. Mag. for February 1867, p. 130.

glacial epoch, a conclusion which we know from geological evidence is incorrect. Influenced by these considerations, I expressed the opinion that it might yet turn out that between 240,000 and 80,000 years ago was the period of the glacial epoch, and that that epoch of glaciation about 850,000 years ago might be that of the Upper Miocene period.

There are physical reasons of great weight against the opinion that the glacial epoch was so remote as 850,000 years ago. If we place the middle of the glacial epoch 850,000 years back, then we must lengthen out to a corresponding extent the entire geological history of our globe. Sir Charles Lyell considers that when we go back as far as the Lower Miocene formations, we arrive at a period when the marine shells differed as a whole from those now existing. But only 5 per cent. of the shells existing at the commencement of the glacial epoch have since died out. Hence, assuming the rate at which the species change to be uniform, it follows that the Lower Miocene period must be twenty times as remote as the commencement of the glacial epoch. Consequently, if it be 1 million of years since the commencement of the glacial epoch, 20 millions of years, Sir Charles concludes, must have elapsed since the time of the Lower Miocene period, and 60 millions of years since the begininng of the Eocene period, and about 160 millions of years since the Carboniferous period, and about 240 millions of years must be the time which has elapsed since the beginning of the Cambrian period. But, on the other hand, if we refer the glacial epoch to the later period of great excentricity, and take 250,000 years ago as the beginning of that period, then, according to the same mode of calculation, we have 15 millions of years since the beginning of the Eocene period, and 40 millions of years since the Carboniferous period, and 60 millions of years in all since the beginning of the Cambrian period.

A great many considerations seem to show that 850,000 years cannot possibly have elapsed since the glacial epoch, and that we must assign that epoch to the period commencing about 240,000 years ago and extending down to about 80,000 years ago. If the glacial epoch be placed at so remote a period as 850,000 years ago, then it is very probable, as Sir Charles Lyell concludes, that the beginning of the Cambrian period will require to be placed 240 millions of years back. But we have evidence of a physical nature which proves that it is absolutely impossible that the existing order of things, as regards our globe, can date so far back as anything like 240 millions of years. The arguments to which I refer are those which have been advanced by Professor Sir William Thomson at various times. These arguments are well known, and to all who have really given due attention to them

must be felt to be conclusive. It would be superfluous to state them here; I shall, however, for reasons which will presently appear, refer briefly to one of them, and the one which seems to be the most conclusive of all, viz. the argument derived from the limit to the age of the sun's heat.

It is found that 83·4 foot-pounds of heat per second is incident upon a square foot of the earth's surface exposed to the perpendicular rays of the sun. The amount radiated from a square foot of the sun's surface to that incident on a square foot of the earth's surface is as the square of the sun's distance to the square of his radius, or as 46,400 to 1. Consequently 3,869,000 foot-pounds of heat is radiated off every square foot of the sun's surface per second—an amount equal to about 7000 horse-power. The total amount radiated from the whole surface of the sun per annum amounts to 8340×10^{30} foot-pounds. To maintain the present rate of radiation, it would require the combustion of about 1500 lbs. of coal per hour on every square foot of the sun's surface; and were the sun composed of that material, it would be all consumed in less than 5000 years. The opinion that the sun's heat is maintained by combustion cannot be entertained for a single moment. A pound of coal falling into the sun from an infinite distance would produce by its concussion more than 6000 times the amount of heat that would be generated by its combustion.

It is well known that the velocity with which a body falling from an infinite distance would reach the sun would be equal to that which would be generated by a constant force equal to the weight of the body at the sun's surface operating through a space equal to the sun's radius. One pound would at the sun's surface weigh about 28 pounds. Take the sun's radius at 441,000 miles*. The energy of a pound of matter falling into the sun from infinite space would equal that of a 28-pound weight descending upon the earth from an elevation of 441,000 miles, supposing the force of gravity to be as great at that elevation as it is at the earth's surface. It amounts to upwards of 65,000,000,000 foot-pounds. A better idea of this enormous amount of energy exerted by a one-pound weight falling into the sun will be conveyed by stating that it would be sufficient to raise 1000 tons to a height of $5\frac{1}{2}$ miles. It would project the 'Warrior,' fully equipped with guns, stores, and ammunition, over the top of Ben Nevis.

Gravitation is now generally admitted to be the only conceivable source of the sun's heat. But if we attribute the energy of the sun to gravitation as a source, we attribute it to a cause

* I have taken for the volume and mass of the sun the values given in Professor Sir William Thomson's paper, Phil. Mag. vol. viii. (1854).

the value of which can be accurately determined. Prodigious as is the energy of a single pound of matter falling into the sun, nevertheless a range of mountains, consisting of 176 cubic miles of solid rock, falling into the sun would only maintain his heat for a single second. A mass equal to that of the earth would maintain the heat for only 93 years, and a mass equal to that of the sun itself falling into the sun would only afford 33,000,000 years' sun-heat.

Suppose, with Helmholtz, that the sun originally existed as a nebulous mass, filling the entire space presently occupied by the solar system and extending into space indefinitely beyond the outermost planet. The total amount of work in foot-pounds performed by gravitation in the condensation of this mass to an orb of the sun's present size can be found by means of the following formula given by Helmholtz *,

$$\text{Work of condensation} = \frac{3}{5} \cdot \frac{r^2 M^2}{R m};$$

M is the mass of the sun, m the mass of the earth, R the sun's radius, and r the earth's radius. Taking $M = 4230 \times 10^{27}$ lbs., $m = 11,920 \times 10^{21}$ lbs., $R = 2,328,500,000$ feet, and $r = 20,889,272$ feet; we have then for the total amount of work performed by gravitation in foot-pounds,

$$\text{Work} = \frac{3}{5} \cdot \frac{(20,889,272 \cdot 5)^2 \times (4230 \times 10^{27})^2}{2,328,500,000 \times 11,920 \times 10^{21}}$$
$$= 168,790 \times 10^{36} \text{ foot-pounds.}$$

The amount of heat thus produced by gravitation would suffice for nearly 20,237,500 years.

These calculations are based upon the assumption that the density of the sun is uniform throughout. But it is highly probable that the sun's density increases towards the centre. In this case the amount of work performed by gravitation would be somewhat more than the above.

Must we have a greater amount of heat than what could have resulted from gravitation? If so, then what other possible source of energy can there be? There is still another possible source. The foregoing calculation in regard to the total amount of heat radiated from the sun is made upon the assumption that the matter composing the sun, when it existed in space as a nebulous mass, was not originally possessed of temperature, but that the temperature was given to it as the mass became condensed under the force of gravitation. We have supposed the heat given out to be simply the heat of condensation. But it

* Phil. Mag. S. 4. vol. xi. p. 516 (1856).

is quite conceivable that this nebulous mass might have been possessed of an original store of heat previous to condensation. It is quite possible that the very reason why it existed in such a rarefied or gaseous condition was its excessive temperature, and that condensation only began to take place as the mass began to cool down. It seems far more probable that this should have been the case than that the mass existed in so rarefied a condition without temperature. For why should the particles have existed in this separated form when devoid of the repulsive energy of heat, seeing that in virtue of gravitation they had such a tendency to approach to one another? But if the mass was originally in a heated condition, then in condensing it would have to part not only with the heat generated in condensing, but also with the heat which it originally possessed, a quantity which would no doubt much exceed that produced by condensation. To illustrate this principle, let us suppose a pound of air, for example, to be placed in a cylinder and heat applied to it. If the piston be so fixed that it cannot move, 234·5 foot-pounds of heat will raise the temperature of the air 1° C. But if the piston be allowed to rise as the heat is applied, then it will require 330·2 foot-pounds of heat to raise the temperature 1° C. It requires 95·7 foot-pounds more heat in the latter case than in the former. The same amount of energy, viz. 234·5 foot-pounds, in both cases goes to produce temperature; but in the latter case, where the piston is allowed to move, 95·7 foot-pounds of additional heat is consumed in the mechanical work of raising the piston. Suppose, now, that the air is allowed to cool under the same conditions : in the one case 234·5 foot-pounds of heat will be given out while the temperature of the air sinks 1° C.; in the other case, where the piston is allowed to descend, 330·2 foot-pounds will be given out while the temperature sinks 1° C. In the former case, the air in cooling has simply to part with the energy which it possesses in the form of temperature; but in the latter case it has, in addition to this, to part with the energy bestowed upon its molecules by the descending piston. While the temperature of the gas is sinking 1°, 95·7 foot-pounds of energy in the form of heat is being imparted to it by the descending piston; and this has to be got rid of before the temperature is lowered by 1°. Consequently 234·5 foot-pounds of the heat given out previously existed in the air under the form of temperature, and the remaining 95·7 foot-pounds given out was imparted to the air by the descending piston while the gas was losing its temperature. 234·5 foot-pounds is the energy or heat which the air previously possessed, and 95·7 is the energy or heat of condensation.

In the case of the cooling of the sun from a nebulous mass,

there would of course be no external force or pressure exerted on the mass analogous to that of the piston on the air; but there would be, what is equivalent to the same, the gravitation of the particles to each other. There would be the pressure of the whole mass towards the centre of convergence. In the case of air, and all perfect gases cooling under pressure, about 234 foot-pounds of the original heat possessed by the gas is given out while 95 foot-pounds is generated by condensation. We have, however, no reason whatever to believe that in the case of the cooling of the sun the same proportions would hold true. The proportion of original heat possessed by the mass of the sun to that produced by condensation may have been much greater than 234 to 95, or it may have been much less. In the absence of all knowledge on this point, we may in the meantime assume that to be the proportion. The total quantity of heat given out by the sun resulting from the condensation of his mass, on the supposition that the density of the sun is uniform throughout, we have seen to be equal to 20,237,500 years' sun-heat. Then the quantity of heat given out, which previously existed in the mass as original temperature, must have been 49,850,000 years' heat. In all, 70,087,500 years' heat as the total amount.

The above quantity represents, of course, the total amount of heat given out by the mass since it began to condense. But the geological history of our globe must date its beginning to a period posterior to that. For at that time the mass would probably occupy a much greater amount of space than is presently possessed by the entire solar system; and consequently, before it had cooled down to within the limits of the earth's present orbit, our earth could not have had an existence as a separate planet. Previously to that time it must have existed as a portion of the sun's fiery mass. If we assume that it existed as a globe previously to that, and came in from space after the condensation of the sun, then it is difficult to conceive how its orbit should be so nearly circular as it is at present.

Let us assume that by the time that the mass of the sun had condensed to within the space encircled by the orbit of the planet Mercury (that is, to a sphere having, say, a radius of 18,000,000 miles) the earth's crust began to form; and let this be the time when the geological history of our globe dates its commencement. The total amount of heat generated by the condensation of the sun's mass from a sphere of this size to its present volume would equal 19,740,000 years' sun-heat. The amount of original heat given out during that time would equal 48,625,000 years' sun-heat,—thus giving a total of 68,365,000 years' sun-heat enjoyed by our globe since that period. The total quantity may possibly, of course, be considerably more than that, owing

to the fact that the sun's density may increase greatly towards his centre.   But we should require to make extravagant assumptions regarding the interior density of the sun and the proportion of original heat to that produced by condensation before we could manage to account for anything like the period that geological phenomena are supposed by some to demand.

There seems to be an impression on the mind of a great many geologists, that, notwithstanding all that has been advanced regarding the limitation to the age of the sun's heat, there may yet be found some possible way of accounting for a duration of sun-heat equal to a few million of centuries.

If the sun has really given out some two or three hundred million years' heat, one of three things must follow : (1) the sun must have been in possession of that enormous store of energy prior to the commencement of the geological history of our globe ; or (2) he must have received it after the commencement ; or (3) a part must have been originally possessed by the sun prior to the commencement, and the rest derived afterwards. We must admit that one or other of these three suppositions is true ; for these exhaust the whole field of the possible.   But if the sun had originally possessed the amount of energy supposed, then his volume would have extended beyond our earth's orbit, and, of course, our earth could not at that time have existed as a separate planet.   That amount of energy could not have been imparted to the sun since the commencement of our globe's geological history.   It could not under any conditions have been communicated by chemical agency, nor by any means conceivable except by that of meteors or other bodies falling into the sun with enormous velocity.   And if we suppose gravitation to be the agent that gave these bodies their velocity, then it is found by calculation that gravitation falls far short of affording the necessary amount of velocity.   If we adopt the third supposition, that part of the energy was originally possessed by the sun, and part imparted, this will not remove the difficulty ; for as the energy imparted by gravitation could be only but a small fraction of the amount required, the hundreds of millions of years' heat demanded, with the exception of that portion imparted, must have been in the possession of the sun at the commencement of our globe's geological history.   But the sun cannot, as we have seen, have been a sphere with the earth revolving round it as a planet if it was in possession of such a store of energy ; for its volume would have more than filled the entire space encircled by the earth's orbit.

It is quite possible, however, that a meteor may reach the sun with a velocity far greater than that which it could acquire by gravitation ; for it might have been moving in a direct line to-

wards the sun with an original velocity before coming under the sensible influence of the sun's attraction. In this case a greater amount of heat would be generated by the meteor than would have resulted from its merely falling into the sun under the influence of gravitation. But then meteors of this sort must be of rare occurrence. And we have but very little warrant on this ground to conclude that the amount of energy communicated to the sun since the geological history of our globe began could have been much more than the equivalent of the work performed by gravitation in the condensation of his mass.

It is highly probable, as Professor Sir William Thomson has concluded, that the sun in the early geological periods must have been far hotter than at present, owing to his excessively high temperature. When the sun's mass was in an intensely heated condition, filling perhaps the entire sphere occupied by the planetary system, it would no doubt be in a gaseous state, and of excessively small density. Gases are known to be bad radiators; and it is probable that a gaseous mass of such rarity would radiate its heat into space with some difficulty; and this might tend in a great measure to lessen the excessive rate of radiation which would otherwise result from so prodigious a temperature.

The question naturally suggests itself, how could the sun's mass have been originally raised to such a high temperature as we have assumed? What power could raise the temperature of the sun's mass to such an extent as to cause it to become an incandescent gas of such rarity? By what means could this mass become possessed of 50,000,000 years' heat, as we have concluded, even before it began to condense? There is nothing at all absurd or improbable in the supposition that such an amount of energy might have been communicated to the mass. The Dynamical Theory of Heat affords an easy explanation of at least *how* such an amount of energy *may* have been communicated. Two bodies, each one-half the mass of the sun, moving directly towards each other with a velocity of 476 miles per second, would by their concussion generate in a *single moment* the 50,000,000 years' heat. For two bodies of that mass moving with a velocity of 476 miles per second would possess 4149×10^{38} foot-pounds of energy in the form of *vis viva*; and this, converted into heat by the stoppage of their motion, would give an amount of heat which would cover the present rate of the sun's radiation for a period of 50,000,000 years.

Why may not the sun have been composed of two such bodies? And why may not the original store of heat possessed by him have all been derived from the concussion of these two bodies? Two such bodies coming into collision with that velocity would be dissipated into vapour by such an inconceivable

amount of heat as would thus be generated; and when they condensed on cooling, they would form one spherical mass like the sun. It is perfectly true that two such bodies could never attain the required amount of velocity by their mutual gravitation towards each other. But there is no necessity whatever for supposing that their velocities were derived from their mutual attraction alone. They might have been approaching towards each other with the required velocity wholly independent of gravitation.

We know nothing whatever regarding the absolute motion of bodies in space. And beyond the limited sphere of our observation, we know nothing regarding even their relative motions. There may be bodies moving in relation to our system with inconceivable velocity. For anything that we know to the contrary, were one of these bodies to strike our earth, the shock might be sufficient to generate an amount of heat that would dissipate the earth into vapour, though the striking body might not be heavier than a cannon-ball. There is, however, nothing very extraordinary in the velocity which we have found would be required in the two supposed bodies to generate the 50,000,000 years' heat. A comet, having an orbit extending to the path of the planet Neptune, approaching so near the sun as to almost graze his surface in passing, would have a velocity of about 390 miles per second, which is within 86 miles of the required velocity.

But in the original heating and expansion of the sun into a gaseous mass, an amount of work must have been performed against gravitation equal to that which has been performed by gravitation during his cooling and condensation, a quantity which we have found amounts to about 20,000,000 years' heat. The total amount of energy originally communicated by the concussion must have been equal to 70,000,000 years' sun-heat. A velocity of 563 miles per second would give this amount. All, however, that is intended by this hypothesis is merely to show how easy it is to explain how the sun may originally have become an incandescent gas filling the entire space occupied by the planetary system.

But is it the case that geology really requires such enormous periods as is generally supposed? At present, geological estimates of time are little else than mere conjectures. Geological science has hitherto afforded no trustworthy means of estimating the positive length of geological epochs. Geological phenomena tell us most emphatically that these periods must be long; but how long, these phenomena have, as yet, failed to inform us. Geological phenomena represent time to the mind under a most striking and imposing form. They present to the eye, as it were,

a sensuous representation of time; the mind thus becomes deeply impressed with a sense of immense duration; and when one under these feelings is called upon to put down in figures what he believes will represent that duration, he is very apt to be deceived. If, for example, a million of years as represented by geological phenomena and a million of years as represented by figures were placed before our eyes, we should certainly feel startled. We should probably feel that a unit with six ciphers after it was really something far more formidable than we had hitherto supposed it to be. Could we stand upon the edge of a gorge a mile and a half in depth that had been cut out of the solid rock by a tiny stream, scarcely visible at the bottom of this fearful abyss, and were we informed that this little streamlet was able to wear off annually only $\frac{1}{10}$ of an inch from its rocky bed, what would our conceptions be of the prodigious length of time that this stream must have taken to excavate the gorge? We should certainly feel startled when, on making the necessary calculations, we found that the stream had performed this enormous amount of work in something less than a million of years.

If we could possibly form some adequate conception of a period so prodigious as one hundred millions of years, we should not then feel so dissatisfied at being told that the age of the earth's crust is not greater than that.

Here is one way of conveying to the mind some idea of what a million of years really is. Take a narrow strip of paper an inch broad, or more, and 83 feet 4 inches in length, and stretch it along the wall of a large hall, or round the walls of an apartment somewhat over 20 feet square. Recall to memory the days of your boyhood, so as to get some adequate conception of what a period of a hundred years is. Then mark off from one of the ends of the strip $\frac{1}{10}$ of an inch. The $\frac{1}{10}$ of the inch will then represent one hundred years, and the entire length of the strip a million of years. It is well worth making the experiment, just in order to feel the striking impression that it produces on the mind.

The methods which have been adopted in estimating geological time not only fail to give us the positive length of geological periods, but some of them are actually calculated to mislead. The method of calculating the length of a period from the thickness of the stratified rocks belonging to that period can give no reliable estimate; for the thickness of the deposit will depend upon a great many circumstances, such as whether the deposition took place near to land or far away in the deep recesses of the ocean, whether it took place at the mouth of a great river or along the sea-shore, whether it took place when the sea-bottom was rising, subsiding, or remaining stationary.

Stratified formations 10,000 feet in thickness, for example, may, under some conditions, have been formed in as many years, while under other conditions it may have required as many centuries.   Nothing whatever can be safely inferred as to the absolute length of a period from the thickness of the stratified formations belonging to that period.   Neither will this method give us a trustworthy estimate of the *relative* lengths of geological periods.   Suppose we find the average thickness of the Cambrian rocks to be 26,000 feet, the Silurian to be 28,000 feet, the Devonian to be 6000 feet, and the Tertiary to be 10,000 feet, it would not be safe to assume, as is sometimes done, that the relative duration of those periods must have corresponded to these numbers.   Were we sure that we had got the correct average thickness of all the rocks belonging to each of those formations, we might probably be able to arrive at the relative lengths of those periods ; but we can never be sure of this.   Those formations all, at one time, formed sea-bottoms ; and we can only measure those deposits that are now raised above the sea-level.   But is it not probable that the relative positions of sea and land during the Cambrian, Silurian, Old-Red-Sandstone, Carboniferous, and other early periods of the earth's history differed more from the present relative positions than the relative positions of sea and land during the Tertiary period differed from the relative positions which obtain at present ? May not the greater portion of the Tertiary deposits be still under the sea-bottom ? And if this be the case, it may yet be found at some day in the distant future, when these deposits are elevated into dry land, that they are much thicker than we now conclude them to be.   Of course it is by no means asserted that they are thicker than we conclude them to be.   It is simply asserted that they *may* be thicker for anything that we know to the contrary ; and the possibility that they may, destroys our confidence in the accuracy of this method of determining the relative lengths of geological periods.

  The palæontological method of estimating geological time, either absolute or relative, from the rate at which species change appears to be even still more unsatisfactory.   If we could ascertain by some means or other the time that has elapsed from some given epoch (say, for example, the glacial) till the present day, and were we sure at the same time that species have changed at a uniform rate during all past ages, then, by ascertaining the percentage of change that has taken place since the glacial epoch, we should have a means of making something like a rough estimate of the length of the various periods.   But without some such period to start with, the palæontological method is useless.   It will not do to take the historic period as a base-line.

It is far too short to be used with safety in determining the distance of periods so remote as those which concern the geologist. But even supposing the palæontologist had a period of sufficient length measured off correctly to begin with, his results would still be unsatisfactory ; for it is perfectly obvious, that unless the climatic conditions of the globe during the various periods were nearly the same, the rate at which the species change would certainly not be uniform. But we have evidence, geological as well as cosmical, that the climate of our globe has at various periods undergone changes of the most excessive character.

The palæontological method, as we have already seen, will give 60 millions of years or 240 millions of years as the period that has elapsed since the commencement of the Cambrian period, just as we choose to adopt 250,000 years ago or 1,000,000 years ago as the commencement of the glacial epoch.

It is the modern and philosophic doctrine of uniformity that has chiefly led geologists to overestimate the length of geological periods. This philosophic school teaches, and that truly, that the great changes undergone by the earth's crust must have been produced not by great convulsions and cataclysms of nature, but by those ordinary agencies that we see at work every day around us, such as rain, snow, frost, ice, and chemical action, &c. It teaches that the valleys were not produced by violent dislocations, nor the hills by sudden upheavals, but that they were actually carved out of the solid rock by the silent and gentle agency of chemical action, frost, rain, ice, and running water. It teaches, in short, that the rocky face of our globe has been carved into hill and dale, and ultimately worn down to the sea-level, by means of these apparently trifling agents, not only once or twice, but probably dozens of times over during past ages. Now, when we reflect that with such extreme slowness do these agents perform their work, that we might watch their operations from year to year, and from century to century, if we could, without being able to perceive that they make any very sensible advance, we are necessitated to conclude that geological periods must be enormous. And the conclusion at which we thus arrive is undoubtedly correct. It is, in fact, impossible to form an adequate conception of the length of geological time. It is something too vast to be fully grasped by our conceptions. What those to whom we have been alluding err in is not in forming too great a conception of the extent of geological periods, but in the way in which they represent the length of these periods in numbers. When we speak of units, tens, hundreds, thousands, we can form some notion of what these quantities represent ; but when we come to millions, tens of mil-

lions, hundreds of millions, thousands of millions, the mind is then totally unable to follow, and we can only use these numbers as representations of quantities that turn up in calculation. We know, from the way in which they do turn up in our process of calculation, whether they are correct representations of things in actual nature or not; but we could not, from a mere comparison of these quantities with the thing represented by them, say whether they were actually too small or too great. It is here that some geologists have erred: they have not made the necessary calculations, and found by the known rules of arithmetic that 100,000,000 is too small a number to represent in years the probable age of the earth's crust; but they look first at the phenomena and then at the figures; and as the two produce totally different impressions, they pronounce the figures to be too small to represent the phenomena.

If the geologist could find a method of ascertaining the actual rate at which these denuding agents do perform their work; if it could be ascertained at what rate the face of the country is at present being denuded, how much, for example, per annum the general level of the country is being lowered and the valleys deepened, then we should have a means of ascertaining whether or not the agents to which we refer were really capable of producing the required amount of change in the earth's surface in the allotted time. But mere conjectures in the absence of some positive determinations are worse than useless.

But happily there is a method of ascertaining, with the most perfect accuracy, the rate at which the face of the globe is being denuded by subaërial agency. And it is somewhat remarkable that this method has been so long overlooked by geologists. The method to which I allude is that which has already been incidentally referred to, viz. that of determining the amount of solid materials which is being carried down annually by our rivers into the sea. Were it ascertained (and this might be easily done) how much sediment is being carried down by our rivers into the sea, then we should be able to determine exactly the extent to which the area of drainage of those rivers was being lowered annually by subaërial denudation; for the material carried down by those rivers must all be derived from the surface of the country drained by them. When I published the result of my calculations, from the amount of sediment carried down by the Mississippi, regarding the rate at which the North-American continent is being lowered by denudation, I was not at the time aware that Mr. Alfred Tylor had arrived at somewhat similar results by the self-same method nearly fifteen years ago[*]. His object was to show that the relative level of the

* Phil. Mag. S. 4, vol. v. (1853).

sea is being affected by the transference of sediment from the land to the sea. Such a result, however, is very doubtful; for it is quite possible that it may be more than neutralized by up-heavals of the land.

The amount of sediment carried down into the Gulf of Mexico by the Mississippi River has been estimated with the greatest accuracy by Messrs. Humphreys and Abbot. It is found that the average amount of sediment held in suspension in the waters of the Mississippi is about $\frac{1}{1500}$ of the weight of the water, or $\frac{1}{2900}$ by bulk. The annual discharge of the river is 19,500,000,000,000 cubic feet of water. The quantity of sediment carried down into the Gulf of Mexico amounts to 6,724,000,000 cubic feet. But besides that which is held in suspension, the river pushes down into the sea about 750,000,000 cubic feet of earthy matter, making in all a total of 7,474,000,000 cubic feet transferred from the land to the sea annually. Where does this enormous mass of material come from? Unquestion-ably it comes from the ground drained by the Mississippi. The area drained by the river is 1,244,000 square miles. Now 7,474,000,000 cubic feet removed off 1,224,000 square miles of surface is equal to $\frac{1}{4566}$ of a foot off that surface per annum, or one foot in 4566 years. The specific gravity of the sediment is taken at 1·9, that of rock is about 2·5; consequently the amount removed is equal to one foot of rock in about 6000 years. The average height of the North-American continent above the sea-level, according to Humboldt, is 748 feet; consequently, at the present rate of denudation, the whole area of drainage will be brought down to the sea-level in less than 4,500,000 years* if no elevation of the land takes place.

The rate of denudation of the area drained by the river Ganges is much greater than this. The annual discharge of that river is 6,523,000,000,000 cubic feet of water. The sediment held in suspension is equal $\frac{1}{510}$ by weight; area of drainage 432,480 square miles. This gives 1 foot of rock in 2358 years as the amount removed.

Rough estimates have been made of the amount of sediment carried down by some eight or ten European rivers; and although those estimates cannot be depended upon as being anything like perfectly accurate, still they show (what there is very little reason to doubt) that it is extremely probable that the European conti-nent is being denuded about as rapidly as the American. By means of subaërial agencies continents are cut up into islands,

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* My former estimate was incorrect. It was derived from imperfect data obtained previously to the observations of Humphreys and Abbot. And, besides, I omitted to take into account the difference between the specific gravity of sediment and rock.

the islands into smaller islands, and so on till the whole ultimately disappears.

There can be no doubt about the rate at which the American continent is being denuded by subaërial agency. The sediment carried down into the Gulf of Mexico assuredly comes all off the land. It is not derived from the banks of the river itself, as has been clearly shown by Mr. Tylor. "The Mississippi," he says, "must draw its vast supplies of mud from its tributaries; for it could obtain them from no other source, unless we suppose it abstracts them from its own plains. Certainly in many places soil is being removed from one part or other of its plains; but an equal quantity must be added to some other part; for the river could not make a permanent inroad into its plains without enlarging its channel. This it does not do, or it would be able to carry off the winter freshets without overflowing, and the present artificial bank would be unnecessary."

Every river running through an alluvial plain will cut a channel for itself of a definite capacity, which capacity will be determined by the volume and velocity of the river. If you attempt to increase the size of the channel, it will silt up and assume its former capacity. Or if you attempt to diminish its channel by throwing in loose materials, the river will remove these. We have a good example in the river Clyde of the tendency of a river to preserve its normal size of channel. It is necessary for commercial purposes that the channel of the river below the city of Glasgow should be kept much deeper than the volume and velocity of the river necessarily demands, and the consequence is that it requires the continued efforts of several powerful dredging-machines to counteract the tendency that this little river has to silt up to its normal depth and size of channel.

So long as the present order of things remains, the rate of denudation will continue while land remains above the sea-level; and we have no warrant for supposing that the rate was during past ages less than it is at the present day. It will not do as an objection to say that, as a considerable amount of the sediment carried down by rivers is boulder-clay and other materials belonging to the ice-age, the total amount removed by the rivers is on that account greater than it would otherwise be. Were this objection true, it would follow that, prior to the glacial period, when it is assumed that there was no boulder-clay, the face of the country must have consisted of bare rock; for in this case no soil could have accumulated from the disintegration and decomposition of the rocks, *since, unless the rocks of a country disintegrate more rapidly than the river-systems are able to carry the disintegrated materials to the sea, no surface-soil can form on that country.* The rate at which rivers carry down sediment is evidently not

·determined by the rate at which the rocks are disintegrated and decomposed, but by the quantity of rain falling, and the velocity with which it moves off the face of the country. Every river-system possesses a definite amount of carrying-power, depending upon the slope of the ground, the quantity of rain falling per annum, the manner in which the rain falls, whether it falls gra-·dually or in torrents, and a few other circumstances. When it so happens, as it generally does, that the amount of rock disin-tegrated on the face of the country is greater than the carrying-power of the river-systems can remove, then a soil necessarily forms. But when the reverse is the case no soil can form on that country, and it will present nothing but barren rock. This ·is no doubt the reason why in places like the Island of Skye, for example, where the rocks are exceedingly hard and difficult to decompose and separate, the ground steep, and the quantity of rain falling very great, there is so much bare rock to be seen. If, prior to the glacial epoch, the rocks of the area drained by the Mississippi would not produce annually more material from their destruction under atmospheric agency than was being carried down by that river, then it follows that the country must have presented nothing but bare rock, if the amount of rain falling was then as great as at present.

No proper estimate has been made of the quantity of sediment carried down into the sea by our British rivers. But, from the principles just stated, we are warranted to infer that it must be as great in proportion to the area of drainage as that carried down by the Mississippi. For example, the river Tay, which drains a great portion of the central Highlands of Scotland, car-ries to the sea three times as much water in proportion to its area of drainage as is carried by the Mississippi. And any one who has seen this rapidly running river during a flood, red and turbid with sediment, will easily be convinced that the quantity of solid material carried down by it into the German Ocean must be very great. Mr. John Dougall has found that the waters of the Clyde during a flood hold in suspension $\frac{1}{800}$ by bulk of sedi-ment. The observations were made about a mile above the city of Glasgow. But even supposing (what is certainly an under-estimate) the amount of sediment held in suspension by the waters of the Tay to be only one-third of that of the Mississippi, viz. $\frac{1}{4500}$ by weight, still this would give the rate of denudation of the central Highlands at 1 foot in 6000 years, or 1000 feet in 6 millions of years[*].

But, after all, one foot removed off the general level of the

[*] See a valuable paper by Mr. Archibald Geikie on "Denudation as a measure of Geological Time," which will shortly be published in the Trans-actions of the Glasgow Geological Society.

country since the creation of man, according to Mosaic chrono-
logy, is certainly not a very great quantity.   No person but one
who had some preconceived opinions to maintain would ever
think of concluding that one foot of soil during 6000 years was
an extravagant quantity to be washed off the face of the country
by rain and floods during that long period.   Those who re-
side in the country and are eye-witnesses of the actual effects
of heavy rains upon the soil, our soft country roads, ditches,
burns, and rivers, will have considerable difficulty in actually
believing that only one foot has been washed away during the
past 6000 years.

Some may probably admit that a foot of soil may be washed
off during a period so long as 6000 years, and may tell us that
what they deny is not that a foot of loose and soft soil, but a
foot of solid rock can be washed away during that period.   But
a moment's reflexion must convince them that, unless the rocks
of the country were disintegrating and decomposing as rapidly
into soil as the rain is carrying the soil away, the surface of the
country would ultimately become bare rock.   It is true that the
surface of our country in many places is protected by a thick
covering of boulder-clay; but when this has once been removed,
the rocks will then disintegrate far more rapidly than they are
doing at present.

But slow as is the rate at which the country is being denuded,
yet when we take into consideration a period so enormous as 6
millions of years, we find that the results of denudation are really
startling.   One thousand feet of solid rock during that period
would be removed from off the face of the country.   But if the
mean level of the country would be lowered 1000 feet in 6 mil-
lions of years, how much would our valleys and glens be deepened
during that period?   This is a problem well worthy of the con-
sideration of those who treat with ridicule the idea that the ge-
neral features of our country have been carved out by subaërial
agency.

In consequence of the retardation of the earth's rotation, oc-
casioned by the friction of the tidal-wave, the sea-level must be
slowly sinking at the equator and rising at the poles.   But it
is probable that the land at the equator is being lowered by
denudation as rapidly as the sea-level is sinking.   Nearly one
mile must have been worn off the equator during the past 12
millions of years, if the rate of denudation all along the equator
be equal to that of the basin of the Ganges.

But if the rate of denudation be at present so great, what
must it have been during the glacial epoch?   It must have been
something enormous.   At present, denudation is greatly retarded
by the limited power of our river-systems to remove the loose

materials resulting from the destruction of the rocks. These materials accumulate and form a thick soil over the surface of the rocks, which protects them, to a great extent, from the weathering effects of atmospheric agents. So long as the amount of rock disintegrated exceeds that which is being removed by the river-systems, the soil will continue to accumulate till the amount of rock destroyed per annum is brought to equal that which is being removed. It therefore follows from this principle that the *carrying-power of our river-systems is the true measure of denudation.* But during the glacial epoch the thickness of the soil would have but little effect in diminishing the waste of the rocks ; for at that period the rocks were not decomposed by atmospheric agency, but were ground down by the mechanical friction of the ice. But the presence of a thick soil at this period, instead of retarding the rate of denudation, would tend to increase it tenfold, for the soil would then be used as grinding-material for the ice-sheet. In places where the ice was, say, 2000 feet in thickness, the soil would be forced along over the rocky face of the country, exerting a pressure on the rocks equal to 50 tons on the square foot.

It is true that the rate at which many kinds of rocks decompose and disintegrate is far less than what has been concluded is the mean rate of denudation of the whole country. This is evident from the fact which has been adduced by some writers, that inscriptions on stones which have been exposed to atmospheric agency for a period of 2000 years, or so, have not been obliterated. But in most cases epitaphs on monuments and tombstones, and inscriptions on the walls of buildings, 200 years old, can hardly be read. And this is not all : the stone on which the letters were cut has during that time been rotted in probably to the depth of several inches ; and during the course of a few centuries more the whole mass will crumble into dust.

The facts which we have been considering show also how trifling is the amount of denudation effected by the sea in comparison with that by subaërial agents. The entire sea-coast of the globe, according to Mr. Keith Johnston, is 116,531 miles. Suppose we take the average height of the coast-line at 25 feet, and take also the rate at which the sea is advancing on the land at 1 foot in 100 years, then this gives 15,382,500,000 cubic feet of rock as the total amount removed in 100 years by the action of the sea. The total amount of land is 57,600,000 square miles, or 1,605,750,000,000,000 square feet; and if 1 foot is removed off the surface in 6000 years, then 26,763,000,000,000 cubic feet is removed by subaërial agency in 100 years, or about 1740 times as much as that removed by the sea. Before the sea could

denude the globe as rapidly as the subaërial agents, it would have to advance on the land at the rate of upwards of 17 feet annually.

[To be continued.]

XLIV. *On the Specific Magnetism of Iron.* By Pliny Earle Chase[*].

IN my communication on the numerical relations of gravity and magnetism[†], after adducing various evidences of a correlation that had been long suspected, I endeavoured to obtain approximate valuations for the constant factor K, which was introduced in the comparison of the tidal forces with the force of equilibrium. These approximations led me to " suggest the propriety of considering the element of density (or of its correlative, the square of the time of molecular diffusion), in connexion with both A and M."

In the year after this suggestion was made, Dr. Menzzer announced, as an experimental result (Poggendorff's *Annalen*, November 1865; Phil. Mag. vol. xxx. p. 456), that " the magnetizing-powers of two coils which give the maximum of intensity are as the square roots of their weights."

It therefore appears,

(1) From Graham's and other well-known laws :—

Elasticity $\propto$ specific heat $\propto$ (wave velocity)^2.
Density $\propto$ (time of molecular diffusion)^2.
Weight $\propto$ (time of sonorous vibration)^2.

(2) From observations on terrestrial magnetism :—

Tidal differences $\propto$ (magnetic differences)^2.
Magnetic variation $\propto$ (time)^2.

(3) From Menzzer's experiments :—

Weight $\propto$ (magnetizing-power)^2.

This indirect confirmation of a conjecture which was at first based on a plausible analogy, encourages me to hope that the following comparisons between molecular and cosmical kinetic values may help to explain the specific magnetism of iron.

According to Tredgold, iron may be elongated about $\frac{1}{1400}$ without permanent alteration of structure. Now the ratio, at the earth's surface, of solar terrestrial attraction is about $\frac{1}{1640}$; and four times the ratio of the specific gravity of air to that of iron varies approximately between $\frac{1}{1400}$ and $\frac{1}{1700}$. Although this range of variation is somewhat more than $\frac{1}{5}$ of the least

[*] From Silliman's American Journal for March 1868.
[†] Trans. Amer. Phil. Soc. vol. xiii. p. 126. [Phil. Mag. July 1865, p. 52.]

value, or about $\frac{1}{8000}$ of the total force, it is but little greater than Helmholtz found in the vibration-ratios for the first over-tone of a series of tuning-forks (5·8 to 6·6 times the funda-mental), while it is much less than the daily fluctuation in the terrestrial magnetic force, which appears to be intimately con-nected with the joint action of atmospheric elasticity and solar differential tidal attraction.

The coefficient of atmospheric specific gravity, 4, suggests the ratio of the length of a sonant aërial column to that of an equi-valent sonorous wave, as well as the time of a complete oscillation of each magnetic pulse. During each vibration, from a maximum of condensation across the position of equilibrium to minimum, or *vice versâ*, the effect produced by any constant force would be four times as great as during the half oscillation from either ex-treme to the point of equilibrium. The ratios of wave-velocity to elasticity and density, and of revolution to distance from the centre of motion, point to various experiments upon the relations of magnetic capacity to tenacity in iron, and of magnetizing-power to specific gravity or to specific heat* in coils of different metals. If such experiments should show any intimate con-nexion between elasticity and specific magnetism (a result which it does not seem unreasonable to anticipate), some of the mys-tery in which an interesting physical fact is now shrouded will be happily dispelled.

XLV. *Proceedings of Learned Societies.*

ROYAL SOCIETY.

March 5, 1868.—John Peter Gassiot, Esq., V.P., in the Chair.

THE following communication was read :—
"On Governors." By J. Clerk Maxwell, M.A., F.R.SS.L. & E. A governor is a part of a machine by means of which the velocity of the machine is kept nearly uniform, notwithstanding variations in the driving-power or the resistance.

Most governors depend on the centrifugal force of a piece con-nected with a shaft of the machine. When the velocity increases, this force increases, and either increases the pressure of the piece against a surface or moves the piece, and so acts on a break or a valve.

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* The specific heats of iron, cobalt, and nickel are nearly the same, being each about twenty-seven times that of hydrogen. Recently discovered cos-mical affinities of hydrogen and iron, and the ratio between solar and ter-restrial superficial gravitation, may perhaps sometime lead to the recogni-tion of a significance in relations which would now be generally regarded as fanciful and accidental.

In one class of regulators of machinery, which we may call *modera-tors* *, the resistance is increased by a quantity depending on the velocity.. Thus in some pieces of clockwork the moderator consists of a conical pendulum revolving within a circular case. When the velocity increases, the ball of the pendulum presses against the inside of the case, and the friction checks the increase of velocity.

In Watt's governor for steam-engines the arms open outwards, and so contract the aperture of the steam-valve.

In a water-break invented by Professor J. Thomson, when the velocity is increased, water is centrifugally pumped up, and overflows with a great velocity, and the work is spent in lifting and communicating this velocity to the water.

In all these contrivances an increase of driving-power produces an increase of velocity, though a much smaller increase than would be produced without the moderator.

But if the part acted on by centrifugal force, instead of acting directly on the machine, sets in motion a contrivance which continually increases the resistance as long as the velocity is above its normal value, and reverses its action when the velocity is below that value, the governor will bring the velocity to the same normal value whatever variation (within the working limits of the machine) be made in the driving-power or the resistance.

I propose at present, without entering into any details of mechanism, to direct the attention of engineers and mathematicians to the dynamical theory of such governors.

It will be seen that the motion of a machine with its governor consists in general of a uniform motion, combined with a disturbance which may be expressed as the sum of several component motions. These components may be of four different kinds :—

1. The disturbance may continually increase.
2. It may continually diminish.
3. It may be an oscillation of continually increasing amplitude.
4. It may be an oscillation of continually decreasing amplitude.

The first and third cases are evidently inconsistent with the stability of the motion ; and the second and fourth alone are admissible in a good governor. This condition is mathematically equivalent to the condition that all the possible roots, and all the possible parts of the impossible roots, of a certain equation shall be negative.

I have not been able completely to determine these conditions for equations of a higher degree than the third ; but I hope that the subject will obtain the attention of mathematicians.

The actual motions corresponding to these impossible roots are not generally taken notice of by the inventors of such machines, who naturally confine their attention to the way in which it is *designed* to act ; and this is generally expressed by the real root of the equation. If, by altering the adjustments of the machine, its governing power is continually increased, there is generally a limit at which the disturbance, instead of subsiding more rapidly becomes an oscillating and jerking motion, increasing in violence till it reaches the

* See Mr. C. W. Siemens "On Uniform Rotation," Phil. Trans. 1866, p. 657.

limit of action of the governor. This takes place when the possible part of one of the impossible roots becomes positive. The mathematical investigation of the motion may be rendered practically useful by pointing out the remedy for these disturbances.

This has been actually done in the case of a governor constructed by Mr. Fleeming Jenkin, with adjustments, by which the regulating power of the governor could be altered. By altering these adjustments the regulation could be made more and more rapid, till at last a dancing motion of the governor, accompanied with a jerking motion of the main shaft, showed that an alteration had taken place among the impossible roots of the equation.

I shall consider three kinds of governors, corresponding to the three kinds of moderators already referred to.

In the first kind, the centrifugal piece has a constant distance from the axis of motion, but its pressure on a surface on which it rubs varies when the velocity varies. In the *moderator* this friction is itself the retarding force. In the *governor* this surface is made moveable about the axis, and the friction tends to move it ; and this motion is made to act on a break to retard the machine. A constant force acts on the moveable wheel in the opposite direction to that of the friction, which takes off the break when the friction is less than a given quantity.

Mr. Jenkin's governor is on this principle. It has the advantage that the centrifugal piece does not change its position, and that its pressure is always the same function of the velocity. It has the disadvantage that the normal velocity depends in some degree on the coefficient of sliding friction between two surfaces which cannot be kept always in the same condition.

In the second kind of governor, the centrifugal piece is free to move further from the axis, but is restrained by a force the intensity of which varies with the position of the centrifugal piece in such a way that, if the velocity of rotation has the normal value, the centrifugal piece will be in equilibrium in every position. If the velocity is greater or less than the normal velocity, the centrifugal piece will fly out or fall in without any limit except the limits of motion of the piece. But a break is arranged so that it is made more or less powerful according to the distance of the centrifugal piece from the axis, and thus the oscillations of the centrifugal piece are restrained within narrow limits.

Governors have been constructed on this principle by Sir W. Thomson and by M. Foucault. In the first, the force restraining the centrifugal piece is that of a spring acting between a point of the centrifugal piece and a fixed point at a considerable distance, and the break is a friction-break worked by the reaction of the spring on the fixed point.

In M. Foucault's arrangement, the force acting on the centrifugal piece is the weight of the balls acting downward, and an upward force produced by weights acting on a combination of levers and tending to raise the balls. The resultant vertical force on the balls is proportional to their depth below the centre of motion, which

ensures a constant normal velocity. The break is :—in the first place, the variable friction between the combination of levers and the ring on the shaft on which the force is made to act ; and, in the second place, a centrifugal air-fan through which more or less air is allowed to pass, according to the position of the levers. Both these causes tend to regulate the velocity according to the same law.

The governors designed by the Astronomer Royal on Mr. Siemens's principle for the chronograph and equatorial of Greenwich Observatory depend on nearly similar conditions. The centrifugal piece is here a long conical pendulum, not far removed from the vertical, and it is prevented from deviating much from a fixed angle by the driving-force being rendered nearly constant by means of a differential system. The break of the pendulum consists of a fan which dips into a liquid more or less, according to the angle of the pendulum with the vertical. The break of the principal shaft is worked by the differential apparatus ; and the smoothness of motion of the principal shaft is ensured by connecting it with a fly-wheel.

In the third kind of governor a liquid is pumped up and thrown out over the sides of a revolving cup. In the governor on this principle, described by Mr. C. W. Siemens, the cup is connected with its axis by a screw and a spring, in such a way that if the axis gets ahead of the cup the cup is lowered and more liquid is pumped up. If this adjustment can be made perfect, the normal velocity of the cup will remain the same through a considerable range of driving-power.

It appears from the investigations that the oscillations in the motion must be checked by some force resisting the motion of oscillation. This may be done in some cases by connecting the oscillating body with a body hanging in a viscous liquid, so that the oscillations cause the body to rise and fall in the liquid.

To check the variations of motion in a revolving shaft, a vessel filled with viscous liquid may be attached to the shaft. It will have no effect on uniform rotation, but will check periodic alterations of speed.

Similar effects are produced by the viscosity of the lubricating matter in the sliding parts of the machine, and by other unavoidable resistances ; so that it is not always necessary to introduce special contrivances to check oscillations.

I shall call all such resistances, if approximately proportional to the velocity, by the name of " viscosity," whatever be their true origin.

In several contrivances a differential system of wheelwork is introduced between the machine and the governor, so that the driving-power acting on the governor is nearly constant.

I have pointed out that, under certain conditions, the sudden disturbances of the machine do not act through the differential system on the governor, or *vice versâ*. When these conditions are fulfilled, the equations of motion are not only simple, but the motion itself is not liable to disturbances depending on the mutual action of the machine and the governor.

Distinction between Moderators and Governors.

In regulators of the first kind, let P be the driving-power and R the resistance, both estimated as if applied to a given axis of the machine. Let V be the normal velocity, estimated for the same axis, and $\frac{dx}{dt}$ the actual velocity, and let M be the moment of inertia of the whole machine reduced to the given axis.

Let the governor be so arranged as to increase the resistance or diminish the driving-power by a quantity $F\left(\frac{dx}{dt}-V\right)$, then the equation of motion will be

$$\frac{d}{dt}\left(M\frac{dx}{dt}\right)=P-R-F\left(\frac{dx}{dt}-V\right). \quad \ldots \ldots \quad (1)$$

When the machine has obtained its final rate the first term vanishes, and

$$\frac{dx}{dt}=V+\frac{P-R}{F}. \quad \ldots \ldots \ldots \ldots \quad (2)$$

Hence, if P is increased or R diminished, the velocity will be permanently increased. Regulators of this kind, as Mr. Siemens * has observed, should be called moderators rather than governors.

In the second kind of regulator, the force $F\left(\frac{dx}{dt}-V\right)$, instead of being applied directly to the machine, is applied to an independent moving piece, B, which continually increases the resistance, or diminishes the driving-power, by a quantity depending on the whole motion of B.

If y represents the whole motion of B, the equation of motion of B is

$$\frac{d}{dt}\left(B\frac{dy}{dt}\right)=F\left(\frac{dx}{dt}-V\right), \quad \ldots \ldots \ldots \quad (3)$$

and that of M

$$\frac{d}{dt}\left(M\frac{dx}{dt}\right)=P-R-F\left(\frac{dx}{dt}-V\right)+Gy, \quad \ldots \ldots \quad (4)$$

where G is the resistance applied by B when B moves through one unit of space.

We can integrate the first of these equations at once, and we find

$$B\frac{dy}{dt}=F\left(x-Vt\right); \quad \ldots \ldots \ldots \ldots \quad (5)$$

so that if the governor B has come to rest $x=Vt$, and not only is the velocity of the machine equal to the normal velocity, but the position of the machine is the same as if no disturbance of the driving-power or resistance had taken place.

Jenkin's Governor.—In a governor of this kind, invented by Mr. Fleeming Jenkin, and used in electrical experiments, a centri-

* "On Uniform Rotation," Phil. Trans. 1866, p. 657.

fugal piece revolves on the principal axis, and is kept always at a constant angle by an appendage which slides on the edge of a loose wheel, B, which works on the same axis. The pressure on the edge of this wheel would be proportional to the square of the velocity ; but a constant portion of this pressure is taken off by a spring which acts on the centrifugal piece. The force acting on B to turn it round is therefore

$$F^1 \overline{\frac{dx}{dt}}\Big|^2 - C^1 ;$$

and if we remember that the velocity varies within very narrow limits we may write the expression

$$F\left(\frac{dx}{dt} - V_1\right),$$

where F is a new constant, and V_1 is the lowest limit of velocity within which the governor will act.

Since this force necessarily acts on B in the positive direction, and since it is necessary that the break should be taken off as well as put on, a weight W is applied to B, tending to turn it in the negative direction ; and, for a reason to be afterwards explained, this weight is made to hang in a viscous liquid, so as to bring it to rest quickly.

The equation of motion of B may then be written

$$B\frac{d^2y}{dt^2} = F\left(\frac{dx}{dt} - V_1\right) - Y\frac{dy}{dt} - W, \quad \ldots \ldots \quad (6)$$

where Y is a coefficient depending on the viscosity of the liquid and on other resistances varying with the velocity, and W is the constant weight.

Integrating this equation with respect to *t*, we find

$$B\frac{dy}{dt} = F(x - V_1 t) - Yy - Wt. \quad \ldots \ldots \ldots \quad (7)$$

If B has come to rest, we have

$$x = \left(V_1 + \frac{W}{F}\right)t + \frac{Y}{F}y, \quad \ldots \ldots \ldots \ldots \quad (8)$$

or the position of the machine is affected by that of the governor, but the final velocity is constant, and

$$V_1 + \frac{W}{F} = V, \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (9)$$

where V is the normal velocity.

The equation of motion of the machine itself is

$$M\frac{d^2x}{dt^2} = P - R - F\left(\frac{dx}{dt} - V_1\right) - Gy. \quad \ldots \ldots \quad (10)$$

This must be combined with equation (7) to determine the motion of the whole apparatus. The solution is of the form

$$x = A_1 e^{n_1 t} + A_2 e^{n_2 t} + A_3 e^{n_3 t} + Vt, \quad \ldots \ldots \ldots \quad (11)$$

where n_1, n_2, n_3 are the roots of the cubic equation

$$\mathrm{MB}n^3 + (\mathrm{MY} + \mathrm{FB})n^2 + \mathrm{FY}n + \mathrm{FG} = 0. \quad \ldots \quad (12)$$

If n be a pair of roots of this equation of the form $a \pm \sqrt{-1}b$, then the part of x corresponding to these roots will be of the form

$$e^{at} \cos{(bt + \beta)}.$$

If a is a negative quantity, this will indicate an oscillation the amplitude of which continually decreases. If a is zero, the amplitude will remain constant, and if a is positive, the amplitude will continually increase.

One root of the equation (12) is evidently a real negative quantity. The condition that the real part of the other roots should be negative is

$$\left(\frac{\mathrm{F}}{\mathrm{M}} + \frac{\mathrm{Y}}{\mathrm{B}}\right)\frac{\mathrm{Y}}{\mathrm{B}} - \frac{\mathrm{G}}{\mathrm{B}} = \text{a positive quantity.}$$

This is the condition of stability of the motion. If it is not fulfilled there will be a dancing motion of the governor, which will increase till it is as great as the limits of motion of the governor. To ensure this stability, the value of Y must be made sufficiently great, as compared with G, by placing the weight W in a viscous liquid if the viscosity of the lubricating materials at the axle is not sufficient.

To determine the value of F, put the break out of gear, and fix the moveable wheel; then, if V and V′ be the velocities when the driving-power is P and P′,

$$\mathrm{F} = \frac{\mathrm{P} - \mathrm{P}'}{\mathrm{V} - \mathrm{V}'}.$$

To determine G, let the governor act, and let y and y' be the positions of the break when the driving-power is P and P′, then

$$\mathrm{G} = \frac{\mathrm{P} - \mathrm{P}'}{y - y'}.$$

General Theory of Chronometric Centrifugal Pieces.

Sir W. Thomson's and M. Foucault's Governors.—Let A be the moment of inertia of a revolving apparatus, and θ the angle of revolution. The equation of motion is

$$\frac{d}{dt}\left(\mathrm{A}\frac{d\theta}{dt}\right) = \mathrm{L}, \quad \ldots \ldots \ldots (1)$$

where L is the moment of the applied force round the axis.

Now, let A be a function of another variable ϕ (the divergence of the centrifugal piece), and let the kinetic energy of the whole be

$$\frac{1}{2}\mathrm{A}\overline{\frac{d\theta}{dt}}^2 + \frac{1}{2}\mathrm{B}\overline{\frac{d\phi}{dt}}^2,$$

where B may also be a function of ϕ, if the centrifugal piece is complex.

If we also assume that P, the potential energy of the apparatus,

2 D 2

is a function of ϕ, then the force tending to *diminish* ϕ, arising from the action of gravity, springs, &c., will be $\dfrac{d\mathrm{P}}{d\phi}$.

The whole energy, kinetic and potential, is

$$\mathrm{E}=\frac{1}{2}\,\mathrm{A}\,\overline{\frac{d\theta}{dt}}\Big|^2+\frac{1}{2}\,\mathrm{B}\,\overline{\frac{d\phi}{dt}}\Big|^2+\mathrm{P}=\!\int\!\mathrm{L}d\theta. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Differentiating with respect to t, we find

$$\frac{d\phi}{dt}\Big(\frac{1}{2}\frac{d\mathrm{A}}{d\phi}\overline{\frac{d\theta}{dt}}\Big|^2+\frac{1}{2}\frac{d\mathrm{B}}{d\phi}\overline{\frac{d\phi}{dt}}\Big|^2+\frac{d\mathrm{P}}{d\phi}\Big)+\mathrm{A}\frac{d\theta}{dt}\frac{d^2\theta}{dt^2}+\mathrm{B}\frac{d\phi}{dt}\frac{d^2\phi}{dt^2}\Bigg]$$
$$=\mathrm{L}\frac{d\theta}{dt}=\frac{d\theta}{dt}\Big(\frac{d\mathrm{A}}{d\phi}\frac{d\theta}{dt}\frac{d\phi}{dt}+\mathrm{A}\frac{d^2\theta}{dt^2}\Big), \Bigg\} \quad . \quad . \quad (3)$$

whence we have, by eliminating L,

$$\frac{d}{dt}\Big(\mathrm{B}\frac{d\phi}{dt}\Big)=\frac{1}{2}\frac{d\mathrm{A}}{d\phi}\overline{\frac{d\theta}{dt}}\Big|^2+\frac{1}{2}\frac{d\mathrm{B}}{d\phi}\overline{\frac{d\phi}{dt}}\Big|^2-\frac{d\mathrm{P}}{d\phi}. \quad . \quad . \quad . \quad . \quad (4)$$

The first two terms on the right-hand side indicate a force tending to *increase* ϕ, depending on the squares of the velocities of the main shaft and of the centrifugal piece. The force indicated by these terms may be called the centrifugal force.

If the apparatus is so arranged that

$$\mathrm{P}=\tfrac{1}{2}\,\mathrm{A}\omega^2+\text{const.}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where ω is a constant velocity, the equation becomes

$$\frac{d}{dt}\Big(\mathrm{B}\frac{d\phi}{dt}\Big)=\frac{1}{2}\frac{d\mathrm{A}}{d\phi}\Big(\overline{\frac{d\theta}{dt}}\Big|^2-\omega^2\Big)+\frac{1}{2}\frac{d\mathrm{B}}{d\phi}\overline{\frac{d\phi}{dt}}\Big|^2. \quad . \quad . \quad . \quad . \quad (6)$$

In this case the value of ϕ cannot remain constant unless the angular velocity is equal to ω.

A shaft with a centrifugal piece arranged on this principle has only one velocity of rotation without disturbance. If there be a small disturbance, the equations for the disturbances θ and ϕ may be written

$$\mathrm{A}\frac{d^2\theta}{dt^2}+\frac{d\mathrm{A}}{d\phi}\,\omega\,\frac{d\phi}{dt}=\mathrm{L}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\mathrm{B}\frac{d^2\phi}{dt^2}-\frac{d\mathrm{A}}{d\phi}\,\omega\,\frac{d\theta}{dt}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The period of such small disturbances is $\dfrac{d\mathrm{A}}{d\phi}\,(\mathrm{AB})^{-\frac{1}{2}}$ revolutions of the shaft. They will neither increase nor diminish if there are no other terms in the equations.

To convert this apparatus into a governor, let us assume viscosities X and Y in the motions of the main shaft and the centrifugal

piece, and a resistance $G\phi$ applied to the main shaft. Putting $\dfrac{dA}{d\phi}\,\omega=K$, the equations become

$$A\frac{d^2\theta}{dt^2}+X\frac{d\theta}{dt}+K\frac{d\phi}{dt}+G\phi=L, \quad \ldots \ldots \quad (9)$$

$$B\frac{d^2\phi}{dt^2}+Y\frac{d\phi}{dt}-K\frac{d\theta}{dt}=0. \quad \ldots \ldots \quad (10)$$

The condition of stability of the motion indicated by these equations is that all the possible roots, or parts of roots, of the cubic equation

$$ABn^3+(AY+BX)n^2+(XY+K^2)n+GK=0 \quad . \quad (11)$$

shall be negative ; and this condition is

$$\left(\frac{X}{A}+\frac{Y}{B}\right)(XY+K^2)>GK. \quad \ldots \ldots \ldots \quad (12)$$

Combination of Governors.—If the break of Thomson's governor is applied to a moveable wheel, as in Jenkin's governor, and if this wheel works a steam-valve, or a more powerful break, we have to consider the motion of three pieces. Without entering into the calculation of the general equations of motion of these pieces, we may confine ourselves to the case of small disturbances, and write the equations

$$\left.\begin{aligned}A\frac{d^2\theta}{dt^2}+X\frac{d\theta}{dt}+K\frac{d\phi}{dt}+T\phi+J\psi&=P-R,\\[4pt] B\frac{d^2\phi}{dt^2}+Y\frac{d\phi}{dt}-K\frac{d\theta}{dt}&=0,\\[4pt] C\frac{d^2\psi}{dt^2}+Z\frac{d\psi}{dt}-T\phi&=0,\end{aligned}\right\} \quad . \quad (13)$$

where θ, ϕ, ψ are the angles of disturbance of the main shaft, the centrifugal arm, and the moveable wheel respectively, A, B, C their moments of inertia, X, Y, Z the viscosity of their connexions, K is what was formerly denoted by $\dfrac{dA}{d\phi}\omega$, and T and J are the powers of Thomson's and Jenkin's breaks respectively.

The resulting equation in n is of the form

$$\begin{vmatrix} An^2+Xn & Kn+T & J \\ -K & Bn+Y & 0 \\ 0 & -T & Cn^2+Zn \end{vmatrix}=0, \quad . \quad (14)$$

or

$$\left.\begin{aligned} &n^5+n^4\left(\frac{X}{A}+\frac{Y}{B}+\frac{Z}{C}\right)+n^3\left[\frac{XYZ}{ABC}\left(\frac{A}{X}+\frac{B}{Y}+\frac{C}{Z}\right)+\frac{K^2}{AB}\right]\\[4pt] &+n^2\left(\frac{XYZ+KTC+K^2Z}{ABC}\right)+n\frac{KTZ}{ABC}+\frac{KTJ}{ABC}=0.\end{aligned}\right\} \quad (15)$$

I have not succeeded in determining completely the conditions of stability of the motion from this equation; but I have found two necessary conditions, which are in fact the conditions of stability of the two governors taken separately. If we write the equation

$$n^5 + pn^4 + qn^3 + rn^2 + sn + t, \quad \ldots \ldots \quad (16)$$

then, in order that the possible parts of all the roots shall be negative, it is necessary that

$$pq > r \text{ and } ps > t. \quad \ldots \ldots \ldots \quad (17)$$

I am not able to show that these conditions are sufficient. This compound governor has been constructed and used.

On the Motion of a Liquid in a Tube revolving about a Vertical Axis.

Mr. C. W. Siemens's Liquid Governor.—Let ρ be the density of the fluid, k the section of the tube at a point whose distance from the origin measured along the tube is s, r, θ, z the coordinates of this point referred to axes fixed with respect to the tube, Q the volume of liquid which passes through any section in unit of time. Also let the following integrals, taken over the whole tube, be

$$\int \rho k r^2 ds = A, \quad \int \rho r^2 d\theta = B, \quad \int \rho \frac{1}{a} ds = C, \quad \ldots \ldots \quad (1)$$

the lower end of the tube being in the axis of motion.

Let ϕ be the angle of position of the tube about the vertical axis, then the moment of momentum of the liquid in the tube is

$$H = A \frac{d\phi}{dt} + BQ. \quad \ldots \ldots \ldots \ldots \quad (2)$$

The moment of momentum of the liquid thrown out of the tube in unit of time is

$$\frac{dH'}{dt} = \rho r^2 Q \frac{d\phi}{dt} + \rho \frac{r}{k} Q^2 \cos a, \quad \ldots \ldots \ldots \quad (3)$$

where r is the radius at the orifice, k its section, and a the angle between the direction of the tube there and the direction of motion.

The energy of motion of the fluid in the tube is

$$W = \frac{1}{2} A \overline{\frac{d\rho}{dt}}\bigg|^2 + BQ \frac{d\phi}{dt} + \frac{1}{2} CQ^2 \quad \ldots \ldots \ldots \quad (4)$$

The energy of the fluid which escapes in unit of time is

$$\frac{dW'}{dt} = \rho g Q (h+z) + \frac{1}{2} \rho r^2 Q \overline{\frac{d\phi}{dt}}\bigg|^2 + \rho \frac{r}{k} \cos a Q^2 \frac{d\phi}{dt} + \frac{1}{2} \frac{\rho}{k^2} Q^3. \quad \ldots \quad (5)$$

The work done by the prime mover in turning the shaft in unit of time is

$$L \frac{d\phi}{dt} = \frac{d\phi}{dt} \left(\frac{dH}{dt} + \frac{dH'}{dt} \right). \quad \ldots \ldots \ldots \quad (6)$$

The work spent on the liquid in unit of time is

$$\frac{d\mathrm{W}}{dt} + \frac{d\mathrm{W}'}{dt}.$$

Equating this to the work done, we obtain the equations of motion

$$\mathrm{A}\frac{d^2\phi}{dt^2} + \mathrm{B}\frac{d\mathrm{Q}}{dt} + \rho r^2 \mathrm{Q}\frac{d\phi}{dt} + \rho\frac{r}{k}\cos\alpha\mathrm{Q}^2 = \mathrm{L}, \quad \ldots \ldots \quad (7)$$

$$\mathrm{B}\frac{d^2\phi}{dt^2} + \mathrm{C}\frac{d\mathrm{Q}}{dt} + \tfrac{1}{2}\frac{\rho}{k^2}\,\mathrm{Q}^2 + \rho g(h+z) - \tfrac{1}{2}\rho r^2\overline{\frac{d\phi}{dt}}\Big|^2 = 0. \quad \ldots \quad (8)$$

These equations apply to a tube of given section throughout. If the fluid is in open channels, the values of A and C will depend on the depth to which the channels are filled at each point, and that of k will depend on the depth at the overflow.

In the governor described by Mr. C. W. Siemens in the paper already referred to, the discharge is practically limited by the depth of the fluid at the brim of the cup.

The resultant force at the brim is $f = \sqrt{g^2 + \omega^4 r^2}$.

If the brim is perfectly horizontal, the overflow will be proportional to $x^{\frac{3}{2}}$ (where x is the depth at the brim), and the mean square of the velocity relative to the brim will be proportional to x, or to $\mathrm{Q}^{\frac{2}{3}}$.

If the breadth of overflow at the surface is proportional to x^n, where x is the height above the lowest point of overflow, then Q will vary as $x^{n+\frac{3}{2}}$, and the mean square of the velocity of overflow relative to the cup as x or as $\dfrac{1}{\mathrm{Q}^{n+\frac{3}{2}}}$.

If $n = -\frac{1}{2}$, then the overflow and the mean square of the velocity are both proportional to x.

From the second equation we find for the mean square of velocity

$$\frac{\mathrm{Q}^2}{k^2} = -\frac{2}{\rho}\left(\mathrm{B}\frac{d^2\phi}{dt^2} + \mathrm{C}\frac{d\mathrm{Q}}{dt}\right) + r^2\overline{\frac{d\phi}{dt}}\Big|^2 - 2g(h+r). \quad \ldots \quad (9)$$

If the velocity of rotation and of overflow is constant, this becomes

$$\frac{\mathrm{Q}^2}{k^2} = r^2\overline{\frac{d\phi}{dt}}\Big|^2 - 2g(h+r). \quad \ldots \ldots \quad (10)$$

From the first equation, supposing, as in Mr. Siemens's construction, that $\cos\alpha = 0$ and $\mathrm{B} = 0$, we find

$$\mathrm{L} = \rho r^2 \mathrm{Q}\frac{d\phi}{dt}. \quad \ldots \ldots \ldots \quad (11)$$

In Mr. Siemens's governor there is an arrangement by which a fixed relation is established between L and z,

$$\mathrm{L} = -\mathrm{S}z, \quad \ldots \ldots \ldots \quad (12)$$

whence

$$\frac{\mathrm{Q}^2}{k^2} = r^2\overline{\frac{d\phi}{dt}}\Big|^2 - 2gh + \frac{2g\rho}{\mathrm{S}}\,r^2\mathrm{Q}\frac{d\phi}{dt}. \quad \ldots \ldots \quad (13)$$

If the conditions of overflow can be so arranged that the mean square of the velocity, represented by $\dfrac{Q^2}{k^2}$, is proportional to Q, and if the strength of the spring which determines S is also arranged so that

$$\frac{Q^2}{k^2}=\frac{2g\rho}{S}r^2\omega Q, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

the equation will become, if $2gh=\omega^2 r^2$,

$$0=r^2\left(\overline{\frac{d\phi}{dt}}\Big|^2 - \omega^2\right)+\frac{2g\rho}{S}r^2Q\left(\frac{d\phi}{dt}-\omega\right), \quad . \quad . \quad . \quad . \quad (15)$$

which shows that the velocity of rotation and of overflow cannot be constant unless the velocity of rotation is ω.

The condition about the overflow is probably difficult to obtain accurately in practice; but very good results have been obtained within a considerable range of driving-power by a proper adjustment of the spring. If the rim is uniform, there will be a *maximum* velocity for a certain driving-power. This seems to be verified by the results given at p. 667 of Mr. Siemens's paper.

If the flow of the fluid were limited by a hole, there would be a *minimum* velocity instead of a maximum.

The differential equation which determines the nature of small disturbances is in general of the fourth order, but may be reduced to the third by a proper choice of the value of the mean overflow.

Theory of Differential Gearing.

In some contrivances the main shaft is connected with the governor by a wheel or system of wheels which are capable of rotation round an axis, which is itself also capable of rotation about the axis of the main shaft. These two axes may be at right angles, as in the ordinary system of differential bevel wheels; or they may be parallel, as in several contrivances adapted to clockwork.

Let ξ and η represent the angular position about each of these axes respectively, θ that of the main shaft, and ϕ that of the governor; then θ and ϕ are linear functions of ξ and η, and the motion of any point of the system can be expressed in terms either of ξ and η or of θ and ϕ.

Let the velocity of a particle whose mass is m resolved in the direction of x be

$$\frac{dx}{dt}=p_1\frac{d\xi}{dt}+q_1\frac{d\eta}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

with similar expressions for the other coordinate directions, putting suffixes 2 and 3 to denote the values of p and q for these directions. Then Lagrange's equation of motion becomes

$$\Xi\delta\xi + H\delta\eta - \Sigma m\left(\frac{d^2x}{dt^2}\delta x + \frac{d^2y}{dt^2}\delta y + \frac{d^2z}{dt^2}\delta z\right)=0, \quad . \quad . \quad (2)$$

where Ξ and H are the forces tending to increase ξ and η respectively, no force being supposed to be applied at any other point.

Now putting

$$\delta x = p_1\,\delta\xi + q_1\,\delta\eta, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

and

$$\frac{d^2x}{dt^2} = p_1\frac{d^2\xi}{dt^2} + q_1\frac{d^2\eta}{dt^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

the equation becomes

$$\left(\Xi - \Sigma mp^2\frac{d^2\xi}{dt^2} - \Sigma mpq^2\frac{d^2\eta}{dt^2}\right)\delta\xi + \left(H - \Sigma mpq\frac{d^2\xi}{dt^2} - \Sigma mq^2\frac{d^2\eta}{dt^2}\right)\delta\eta = 0 ; \quad (5)$$

and since $\delta\xi$ and $\delta\eta$ are independent, the coefficient of each must be zero.

If we now put

$$\Sigma(mp^2) = L, \quad \Sigma(mpq) = M, \quad \Sigma(mq^2) = N, \quad \cdot \quad \cdot \quad (6)$$

where

$$p^2 = p_1^2 + p_2^2 + p_3^2, \quad pq = p_1q_1 + p_2q_2 + p_3q_3, \quad \text{and} \quad q^2 = q_1^2 + q_2^2 + q_3^2,$$

the equations of motion will be

$$\Xi = L\frac{d^2\xi}{dt^2} + M\frac{d^2\eta}{dt^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

$$H = M\frac{d^2\xi}{dt^2} + N\frac{d^2\eta}{dt^2}. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

If the apparatus is so arranged that $M = 0$, then the two motions will be independent of each other; and the motions indicated by ξ and η will be about conjugate axes—that is, about axes such that the rotation round one of them does not tend to produce a force about the other.

Now let Θ be the driving-power of the shaft on the differential system, and Φ that of the differential system on the governor; then the equation of motion becomes

$$\Theta\delta\theta + \Phi\delta\phi + \left(\Xi - L\frac{d^2\xi}{dt^2} - M\frac{d^2\eta}{dt^2}\right)\delta\xi + \left(H - M\frac{d^2\xi}{dt^2} - N\frac{d^2\eta}{dt^2}\right)\delta\eta = 0 ; \quad (9)$$

and if

$$\begin{aligned}\delta\xi &= P\delta\theta + Q\delta\phi, \\ \delta\eta &= R\delta\theta + S\delta\phi,\end{aligned} \left.\rule{0pt}{20pt}\right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

and if we put

$$\begin{aligned}L' &= LP^2 + 2MPR && + NR^2, \\ M' &= LPQ + M(PS + QR) + NRS, \\ N' &= LQ^2 + 2MQS && + NS^2,\end{aligned}\left.\rule{0pt}{30pt}\right\} \quad \cdot \quad \cdot \quad \cdot \quad (11)$$

the equations of motion in θ and ϕ will be

$$\begin{aligned}\Theta + P\,\Xi + QH &= L'\frac{d^2\theta}{dt^2} + M'\frac{d^2\phi}{dt^2}, \\ \Phi + R\Xi + SH &= M'\frac{d^2\theta}{dt^2} + N'\frac{d^2\phi}{dt^2}.\end{aligned}\left.\rule{0pt}{30pt}\right\} \quad \cdot \quad \cdot \quad (12)$$

If $M'=0$, then the motions in θ and ϕ will be independent of each other. If M is also 0, then we have the relation

$$\text{LPQ} + \text{NRS} = 0 ; \quad \ldots \ldots \quad (13)$$

and if this is fulfilled, the disturbances of the motion in θ will have no effect on the motion in ϕ. The teeth of the differential system in gear with the main shaft and the governor respectively will then correspond to the centres of percussion and rotation of a simple body, and this relation will be mutual.

In such differential systems a constant force, II, sufficient to keep the governor in a proper state of efficiency, is applied to the axis η, and the motion of this axis is made to work a valve or a break on the main shaft of the machine. $\mathcal{Z}$ in this case is merely the friction about the axis of ξ. If the moments of inertia of the different parts of the system are so arranged that $M'=0$, then the disturbance produced by a blow or a jerk on the machine will act instantaneously on the valve, but will not communicate any impulse to the governor.

GEOLOGICAL SOCIETY.

[Continued from p. 317.]

March 11th, 1868.—Prof. T. H. Huxley, LL.D., F.R.S., President, in the Chair.

The following communication was read ;—

" On the Structure of the Crag-beds of Norfolk and Suffolk, with some observations on their Organic remains.—Part I. Coralline Crag." By Joseph Prestwich, Esq., F.R.S., F.G.S., &c.

The history of the division of the several crag-deposits into three formations—the Mammaliferous, Red, and Coralline Crags—having been recounted, the author stated that for the last thirty years the evidence of their sequence had remained unaltered, the distinction between the Mammaliferous and Red Crags being still purely palæontological, not a single case of superposition having been discovered. Mr. Prestwich then proceeded to the special object of this paper, which was to describe more fully the physical structure of the several crags, and to determine, if possible, the exact relation which the Suffolk Crags bear to the Crag of Norfolk.

Commencing with the Coralline Crag, the author stated that the well-known outlier at Sutton furnishes a base-line and the best clue to its structure and dimensions, showing also the depth to which it has been denuded and replaced by the Red Crag. The Coralline Crag is generally described as consisting of two divisions—an upper one, formed chiefly of the remains of Bryozoa, and a lower one of light-coloured sands with a profusion of shells ; and the author now gave their exact dimensions and his proposed subdivisions, as follows :—

	CHARACTER AND THICKNESS.	LOCALITIES.
Upper Division, 36. ft.	*h.* Sand and comminuted shells, 6 ft.	Sudbourne and Gedgrave.
	g. Comminuted shells and remains of Bryozoa, forming a soft building-stone, 30 ft.	Sutton, Sudbourne, Gedgrave, Iken, Aldboro'.
Lower Division, 47 ft.	*f.* Comminuted shells, with numerous entire small shells, 5 ft.	Sutton, Iken, Orford, High Gedgrave.
	e. Sands with numerous Bryozoa, and some small shells and *Echini*, 12 ft.	Sutton, Broom Hill.
	d. Comminuted shells, large, entire, and double shells, and bands of limestone, 15 ft.	Sutton, Broom Hill, Sudbourne.
	c. Marly beds, with numerous well-preserved and double shells, 10 ft.	Sutton, Ramsholt.
	b. Comminuted shells and Cetacean remains, 4 ft.	Sutton.
	a. Phosphatic nodules and mammalian remains, 1 ft.	Sutton.

Mr. Prestwich then stated the localities at which these subdivisions of the Coralline Crag are exposed, and proceeded to discuss the geographical distribution of the existing species in the several zones, and the present range of the organic remains. He agreed in the opinion that the greater number of the Mammalian remains are extraneous fossils—but regarded those of a whale as truly contemporaneous, and probably also the teeth of the *Rhinoceros* and *Mastodon*, while the bones that are more or less drilled he considered to be derived. The occurrence of a large block of porphyry in the basement-bed at Sutton was considered a proof that a considerable degree of winter cold had been attained at that period, as it would be difficult to account for its presence in that bed except by ice-action; the author also enumerated the physical conditions which seem to be suggested by the mineral character and the structure of the several zones, inferring, from the peculiar mixture of southern forms of life with others of a more northern type, that at this early period the setting-in of conditions of considerable cold had commenced.

With the aid of Mr. Gwyn Jeffreys the author had revised the list of Mollusca from the Coralline Crag; and he gave a Table in which the range of the species in space, depth, and time was given, and an analysis of their synonymy by Mr. Jeffreys. He also discussed the relations of the Coralline Crag, with its foreign equivalents, agreeing in the conclusion that the Crag Noir is a stage older than it, while the destruction of beds of the age of some of the older Crags of Belgium have furnished many of its derived fossils. In conclusion the author described the distribution of sea and land at the period of the deposition of the Coralline Crag, as suggested by the affinities of the fossils of that deposit.

then reproduce the modified colours, and the effect would be imperceptible.

But the result is very different for rays produced by the combustion of various substances in a luminous body. A substance capable of producing, for instance, the ray F, which corresponds to blue and to a wave-length of 486·39 millionths of a millimetre, would change its position in the spectrum, owing to the motion of the star; for while the vibrating molecule which produces it would oscillate in the length of time which is peculiar to it and invariable, the wave itself would be lengthened or shortened by the transport of the radiant-point, and therefore would change its refrangibility; comparing it to the same substance radiating near the observer, a difference would be found in the place of the ray. Thus, if the motion were such that it ought to increase the wave-length by 40·63 millionths of a millimetre, the ray F would pass into the place of the ray E in the spectrum, and the colour would be green. To produce a similar change, the star should have in moving away a velocity of 31,000 kilometres in a second, and, in approaching, a velocity of about 16,000 kilometres. As the earth only traverses about 30·4 kilometres in the same time, the star should have in the first of the two cases a thousand times that velocity.

But our present spectroscopic instruments enable us to measure much smaller intervals. Let us suppose that the spectroscope is one which sharply divides the ray D (which is the case with those I am now using), a difference in position equal to the magnitude of this double ray would doubtless be measurable. Now the two rays D' and D'', according to M. Van der Willigen, are at a distance of 4 ten-millionths of a millimetre. A displacement of this amount (taking the velocity of light at 300,000 kilometres in a second) indicates that the star has a velocity of 304 kilometres in moving away—that is, a velocity ten times that of the earth. Half as much would be sufficient if it were approaching.

These velocities are by no means enormous, but still they are far from those which we must assume from the proper motions of the stars. Thus the star 40 of Eridanus, which has four seconds of proper annual motion in the great circle*, if it were supposed to be at the distance of the stellar parallax of half a second, would only traverse 36 kilometres in a second. The question being very delicate, very accurate means of observation were necessary for determining the absolute position of the rays.

This determination may be made by means of artificial lights used with the spectrometer with a slit; but this means is embarrassing in practice, and presents many inconveniences which need not be detailed here. After several attempts, I have found that we succeed more easily by introducing into the field of the telescope the spectrum and the direct image of the star, and comparing them at a fixed point in the field itself. Either the line F or the line E may be chosen; for they are well known from the systems they belong to (hydrogen and iron lines), so that we can be sure there is no error

* Struve, *Cat. Dorp.* p. 153.

as to the substances to which they belong. The line *b* of magnesium is also very good, especially for coloured stars. These lines ought then to have the same place in the spectra of all the stars as regards their direct image, if they are not displaced by the motion. Let us now come to the results.

The apparatus I have used consists of a spectroscope for direct vision, in which for the slit a cylindrical achromatic lens is substituted. The prism is arranged so that part of the rays forming the luminous line in the focus of the cylindrical lens traverse it and are dispersed, while a small portion is transmitted directly beyond the prism. We thus have in the field of the analyzing telescope two images—one dispersed with the rays well defined, the other white and in line. If the prism is suitably cut, we may have exact coincidence between a dark line and a direct white line, by slight variations in the inclination of the axis of the prism. If this coincidence cannot be obtained (which is the case in certain prisms), it is necessary to place in the eyepiece two micrometric wires, and the distance of the line from the white image is measured as in the case of double stars.

The simple spectroscope may also be used with great advantage, for the light is very bright; but if the prism has great dispersive power, the divergence which it produces in the rays traversing it must be compensated by passing the direct pencil through a concave semilens of such a focus as to have the lines and the image of the star in the same focus. We might dispense with the cylindrical lens; but though it is possible to use the rays, they have never the definition and precision which the lens gives. With the simple spectroscope it is still more easy to make the direct image coincide with any line of the spectrum. Although the apparatus was constructed with the pieces I had at hand, I have found that we can very readily recognize the displacement of the line F, if it is not by an amount greater than its own magnitude—that is, a limit almost equal to that above mentioned; for the line F is not twice as great as the double line D.

With these two kinds of apparatus I have analyzed a great part of the stars up to the third magnitude which are now to be seen in the evening. In each series of observations the luminous band of Sirius was first made to coincide with its line F, so that the white line was exactly divided by a very acute point placed in the field of the eyepiece. This opake point, since it almost completely conceals the white line, facilitates the observation of those spectral lines whose light would be enfeebled by its brilliancy. This result being attained without touching the eyepiece, I directed the telescope to another star to ascertain whether a similar coincidence existed.

After having frequently repeated these comparisons, I arrived at the conclusion that in the case of stars belonging to the type of Sirius *there is no displacement which is appreciable by my means of measurement.* In the case of stars of a different type, like *α* of Orion, I made use of other lines, and particularly the line *b* of magnesium, which is very well defined, after having confirmed the coincidence of

the line F and of the line *b* in those stars in which they are both perceptible, like Aldebaran, Capella, &c. By this means I have ascertained that the line of hydrogen is pretty well marked, even in α of Orion, although it is not so characteristic as in Sirius, and that it occupies the first place of a dark band after a beautiful band of bright lines in the greenish blue. The stars hitherto examined belong to Canis Major, to Orion, to Canis Minor, to Leo, to Triangulum, to the Bear, to Auriga, to Cassiopeia.

The conclusion at which we have attained, though negative, is of great importance ; for we have ascertained that among the stars examined there is none whose proper motion is five or six times as great as that of the earth in its orbit. It is undoubtedly possible that we may find similar motions for others ; but to obtain precision in those I have examined means are necessary which at present are not at my disposal.

As the investigations relative to all the stars are not yet completed, I would have deferred this communication to the Academy until I had finished the examination of the entire heavens, but for a reason which seemed to me important enough to decide me to make it now. In fact the apparatus which I have described appeared to me useful for other circumstances—and especially during solar eclipses, in examining the protuberances.

From what I remember of the luminous intensity observed of these protuberances in Spain in 1860, I strongly doubt whether we should succeed in analyzing them with a spectroscope with a slit, especially with telescopes of small dimensions, which are the only ones used for this purpose in distant expeditions, and which have not the equatorial movement given by a clockwork. Without this movement it would be almost impossible to analyze a protuberance with the slit, while with a direct simple spectroscope it could be easily done, since the field is very extensive. The use of the electric spark or of artificial lights might be avoided by introducing the direct rays of the spectroscope, as I do in the case of stars. The protuberances are small enough to be observed with accuracy like the stars ; in fact in the planet Venus I could very well observe the solar lines by using a moderate magnifying-power and a very dispersive prism.

The corona alone might be observed with the slit ; for it has too great a superficies to enable us to distinguish the lines with the simple spectroscope. But I think that with this instrument the protuberances might be very well analyzed with a telescope of 10 centims. aperture. In any case it would be well to choose a telescope of at least 6 inches ; for the relative intensity of the protuberances is greatly enfeebled by the light of the corona on which they are projected ; moreover it seems that their radiation is more remarkable for its chemical than for its luminous intensity.

I may apologize for this digression, which is inspired by the interest which all men of science take in the remarkable phenomenon we expect next August.—*Comptes Rendus*, March 2, 1868.

ON AN OPTICAL PHENOMENON.
BY PROFESSOR ROBERT BALL, ESQ.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

Perhaps some of your readers may have never noticed the production of the phenomenon of mirage by a source of heat other than that of the sun. It was, however, very vividly shown under the following circumstances.

From the deck of a steamer I was watching the rising moon, when it happened that the line of vision grazed the heated funnel. Instantly the light from the moon appeared reflected from the blackened surface, in fact it was difficult to conceive that the effect was not produced by a brilliant mirror. The moon was distant from the side of the chimney by an angle of about twenty minutes when thus seen. Attention once directed to the matter, the same phenomenon was easily recognized by viewing other sources of light under the same circumstances. Thus were observed a distant lighthouse, the planet Jupiter, and on a subsequent occasion the rising sun.

The appearance is explained by the well-known theory of the ordinary mirage; the necessity of the heated surface in this case was easily verified by noticing that the same phenomenon was not produced by the mast.

<div style="text-align:center">
I am, Sir,
Yours &c.,
ROBERT BALL.
</div>

Royal College of Science for Ireland,
  April 4, 1868.

————

ON AN APPARATUS FOR PROVING THAT THE ELECTRIC SPARK DOES NOT PASS THROUGH AN ABSOLUTE VACUUM. BY MM. ALVERGNIAT.

The tubes for this experiment have two platinum wires at a distance of 2 millims. An almost absolute vacuum is produced in them by means of the mercury air-pump which we have constructed. Half an hour is sufficient for this purpose. The tube is then heated to dull redness, either by means of charcoal or by means of a furnace for organic analysis. The latter means renders it possible to raise the heat slowly and gradually to redness without incurring the danger of cracking the tube. When the tube begins to glow we continue to exhaust, and allow the spark to pass until it ceases to do so. The connexion of the tube with the lamp is then broken by sealing it.

In a tube so arranged, notwithstanding the slight distance between both platinum points, the passage of electricity completely stops.— *Comptes Rendus,* vol. lxv. p. 963.

XLVII. *On the Second Fundamental Theorem of the Mechanical Theory of Heat; a Lecture delivered before the Forty-first Meeting of the German Scientific Association, at Frankfort on the Maine, September 23, 1867. By* R. Clausius, *Professor of Physics in the University of Würzburg**.

HAVING been honoured with a requisition to deliver a discourse to the present general meeting of the Association, I have felt it incumbent upon me to choose as my theme, not the result of any special investigation, but some subject of wide application and general interest. I will therefore take the liberty of giving, as briefly and in as easily intelligible a form as possible, an account of the theorem known as the Second Fundamental Theorem of the Mechanical Theory of Heat, which forms one of the two great principles whereon this whole theory is based. It is obvious that it is impossible for me upon the present occasion to present this theorem in a mathematical form, or to give a strict proof of its truth, and to follow out individually its numerous applications; all I can do is to place its meaning and its connexion with the first fundamental theorem of the mechanical theory of heat in a clear light, and perhaps to illustrate by a few examples the conclusions which may be deduced from it.

It is well known that rather more than twenty years ago, following upon the isolated and more general statements of various earlier authors, Mayer of Heilbronn distinctly asserted, and Joule of Manchester proved to demonstration by his experimental investigations, that there exists between mechanical work and

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* Translated from a pamphlet communicated by the Author.

heat a connexion of such a kind that mechanical work can be obtained by the expenditure of heat, and, conversely, heat can be produced by the expenditure of work, there being under all circumstances one constant ratio between the quantity of heat and the amount of work.   This principle, known as the *Principle of the Equivalence of Heat and Work,* formed the starting-point of the rapid development which the mechanical theory of heat has undergone in recent times.

In connexion with this principle, I may be allowed to make a remark which may contribute to facilitate the exposition of what follows.

When work is produced with accompanying expenditure of heat, or heat is produced while work is expended, this may be briefly expressed by saying that heat is transformed into work, or work into heat.   Two such magnitudes, capable of being converted one into the other, so that one of them may serve to replace the other, will naturally often require to be considered together; in a mathematical sense, they must be regarded as of the same kind, and occasions will often arise when it is needful to add them together or subtract them one from the other.   In such cases considerable inconvenience arises from the circumstance that heat and work are measured by reference to different standards.   The unit of work is taken, as is well known, as the product of unit-weight into unit-length, or, for example, on the French metrical system as one kilogrammetre; whereas we are accustomed to take as the unit of heat the quantity of heat which is required to raise the temperature of unit-weight of water from $0°$ to $1°$ C.   While employing these units, we cannot at once speak of the sum of heat and work; in order to make the sum we must either reduce the work to heat-units, or the heat to work-units.   When this is done we always obtain complicated expressions such as these,—"the sum of the heat and the thermal equivalent of the work," or "the sum of the work and the mechanical equivalent of the heat."

On this account I have proposed to introduce, as well as work, a second magnitude, which, while still representing work, expresses it in terms, not of the above-mentioned mechanical unit, but in terms of the unit of heat, and therefore so that that amount of work is taken as the unit of work which is equivalent to the thermal unit.   For work, when thus measured, I have proposed the name *Ergon*[*].   The principle that heat can be converted into ergon and ergon into heat, then, still holds good just as for work, and we have at the same time the simple relation

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[*] [In German *Werk*.   See foot-note to page 253 of the author's 'Mechanical Theory of Heat,' English edition by Hirst (Van Voorst, 1867).—TRANSL.]

that the quantities of heat and ergon which are mutually convertible, and which can therefore replace each other, are expressed by the same numbers. Another convenience is that quantities of heat and ergon can be added together or subtracted from one another without any previous reduction having to be performed upon either the one or the other.

We will consequently in the following discussion always speak of ergon instead of work, and will accordingly call the first fundamental theorem the *Theorem of the Equivalence of Heat and Ergon.*

When once this theorem had been propounded and been confirmed by experiment, it very quickly became generally known ; and we may often find that people who have only a superficial acquaintance with the mechanical theory of heat suppose that it is the sole foundation of this theory. Such a view of it is indicated, for example, by the name which the mechanical theory of heat often goes by in France, namely, *la théorie de l'équivalent mécanique de la chaleur.* There is, however, a second theorem, not included in the first, but one which requires to be separately proved, and which is of as much importance as the other, inasmuch as both theorems together constitute the complete foundation of the mechanical theory of heat.

The fact that this second theorem is less known than the first, and, especially in popular expositions of the mechanical theory of heat, is sometimes passed over in complete silence, is chiefly due to its being much more difficult to understand than the first theorem, since in expounding it we are obliged to discuss conceptions which are then introduced for the first time, and to institute quantitative comparisons between processes which have not previously been considered as mathematical magnitudes. I believe, however, that when once the necessary mode of viewing the subject has become familiar, the second fundamental theorem will appear just as simple and natural as the first.

I will now try to set before you the processes with which we are here concerned, in such a manner that the new kind of comparison may present itself spontaneously as a necessary consequence, and that thus the second fundamental theorem may be clearly seen to be established as well as the first.

If we examine the conditions under which heat can be transformed into ergon, and, conversely, ergon into heat, we find, in the first place, that the commonest and simplest process is the following. The heat which exists in material bodies tends to alter their condition. It tends to expand them, to render solid bodies liquid and gaseous, and, as we may likewise add, to resolve

chemical compounds into their elements. In all these cases the effect of the heat consists in loosening or completely dissolving the connexion which exists between the molecules or atoms, and in separating to the greatest possible distance such molecules as are already completely disconnected from each other.

In order to be able to express this action shortly, I have introduced a magnitude which denotes the extent to which this separation and parting of its smallest particles, which it is the tendency of heat to effect, has already been carried in the case of any body. This magnitude I call the *Disgregation* of the body. The disgregation of a body is consequently, among the three states of aggregation, least in the solid state, greater in the liquid state, and greatest of all in the gaseous state. In the last condition it can still be increased by the molecules separating further from each other—that is, by the gas expanding to a larger volume. In like manner, the decomposition of a chemically compound body into its elements is in general accompanied by an increase of disgregation.

By help of this conception the effect of heat can be simply expressed by saying that *heat tends to increase the disgregation of bodies.*

But in order that the disgregation of a body may be increased, resistances must in most cases be overcome, and resistances of two different kinds. In the first place, in order partially or completely to destroy the connexion between the molecules, the forces with which the molecules mutually attract each other must be overcome ; and in the second place, there are commonly, in addition to these internal forces, other external forces which act upon the body from without. Thus, for example, in order that a body subject to external pressure may expand, this pressure, which opposes an increase of volume, must be overcome. Accordingly heat, when it causes increase of disgregation, must perform internal and external ergon in overcoming the opposing forces. In the performance of this ergon, heat is used up ; and thus *the increase of disgregation involves conversion of heat into ergon.* Conversely, in order to diminish disgregation, ergon (and in general both internal and external ergon) must be expended ; since the forces which in the former case were overcome by heat must now in their turn overcome it. In this process heat is produced ; and we consequently arrive at the result that, *when disgregation is diminished, ergon is transformed into heat.*

For a reason which shall be discussed further on, we will assume provisionally that all the changes we are considering take place in such a way that the inverse changes can take place under exactly the same circumstances. Such changes as these we will, for shortness, call *reversible* changes. This limitation being pre-

supposed, we may say that the quantity of heat converted into ergon when disgregation is increased is exactly the same as the quantity of ergon converted into heat by the corresponding diminution of disgregation.

It will be evident, from what has been said, that between alteration of disgregation on the one hand, and conversion of heat into ergon, or *vice versâ*, on the other hand, there exists a causal connexion, which may be expressed in various ways in the form of a definite law. In order to be able to state this law as simply as possible, we will introduce one more special form of expression.

The process by virtue of which ergon is produced at the expense of heat, or heat is generated at the expense of ergon, has been already spoken of as a *transformation*, heat being said to be transformed into ergon, or ergon into heat. In like manner we may call an alteration of disgregation a *transformation*, the original arrangement of the smallest particles of the body being spoken of as transformed into another arrangement.

Each of these two kinds of transformation can take place in two opposite ways, which can be distinguished from each other by employing the terms *positive* and *negative*. We will regard an increase of disgregation as a positive, and a diminution of disgregation as a negative transformation. And, further, a transformation of ergon into heat shall be reckoned as positive, and the transformation of heat into ergon as negative.

Let us now return to the processes considered above; we then see that when the disgregation of a body is increased (a change which we have agreed to call a positive transformation), a transformation of heat into ergon (which we have agreed to call negative) occurs simultaneously; and in like manner a (negative) diminution of disgregation is accompanied by a (positive) transformation of ergon into heat. Hence we may deduce, as a first conclusion, that *in both cases a positive and a negative transformation take place at the same time*.

But, in considering transformations, it is needful to attend not only to their sign but also to their magnitude. The disgregation of a body may change to a greater or less extent; and in the same way a greater or less quantity of heat may be transformed into ergon, or produced from ergon. Having proper regard to these differences, we may represent the quantitative value of any transformation, when the mode of measuring transformations has been previously determined, by a definite mathematical magnitude, which we will call the *equivalence-value* of the transformation.

The question now arises, in relation to these equivalence-values, whether they are capable of being determined in such a manner that, in the case of every reversible alteration of a body, the

simultaneously occurring positive and negative transformations shall have the same absolute values.

In order that the fulfilment of this condition may be possible, regard must be had, in determining the equivalence-value of a transformation of heat into ergon, or *vice versâ*, to an element of which no mention has hitherto been made. This will be most clearly seen if we take, as an example, a perfect gas as the body through whose changes the transformation in question is brought about.

Let there be given a quantity of a perfect gas occupying some definite volume. If this gas expands to some other volume (say to twice its original volume), an increase of disgregation occurs which is completely determined by the original and final volumes. Moreover the expansion is accompanied by the transformation of heat into ergon. And since no internal ergon is performed in a perfect gas, its molecules being already so far apart that their mutual action may be disregarded, we have to take account only of the external ergon which is exerted in overcoming the external pressure—that is, of ergon which can be easily defined as to magnitude. The heat expended in the production of this quantity of ergon must be imparted to the gas from without, if its temperature is to remain constant.

Let us now assume that the same process, the expansion of the gas from its originally given volume to twice this volume, takes place again at a higher temperature. The pressure of the gas is greater in this case than in the former one, just in the same proportion as its absolute temperature is now higher than it was before. Consequently the amount of ergon that is done, and the quantity of heat expended in producing it, is also greater in the same proportion. Hence in this case, although the increase of disgregation remains the same as before, more heat is transformed into ergon.

The equivalence-values of the transformations of heat into ergon which take place in the two cases must, however, be equal to each other, since the absolute magnitude of each is to be the same as that of the equivalence-value of one and the same change of disgregation. Hence it follows that the equivalence-value of a transformation of heat into ergon depends, not alone on the quantity of heat that is transformed, but also on its temperature; so that in the two cases above supposed, in order to obtain equal equivalence-values for the transformations, the quantities of heat must be divided by the corresponding absolute temperatures.

The way in which the equivalence-values of transformations of heat into ergon, or, conversely, of ergon into heat, are to be determined is thus completely defined. Condensing what has been said as to the sign and absolute magnitude into one short statement, we obtain the following rule :—

To get the equivalence-value of a transformation of heat into ergon, or vice versâ, *prefix to the quantity of heat a positive or negative sign according as it is generated by ergon or is transformed into ergon, and divide by the corresponding absolute temperature.*

It is not needful to consider in detail in this place the way in which the equivalence-value of a change of disgregation can be completely determined; it is sufficient in relation to this point to state a general theorem which contains what is really essential to this determination, as well as the principal result of the investigations, so far as they relate to the question hitherto considered by us. This theorem, in which, in relation to the equivalence-value of the transformation of heat into work, or *vice versâ*, the above rule has been taken as the standard, is as follows :—

The disgregation of every body can be determined in such a manner that it is a magnitude depending solely upon the condition of the body at any moment, and not upon the way by which it came into this condition, and so as further to fulfil the condition that, for every reversible alteration of a body, the alteration of disgregation thereby occasioned and the simultaneous transformation of heat into ergon, or vice versâ, *have equal and opposite equivalence-values, so that their algebraic sum is zero.*

Two simultaneously occurring transformations, however, which have opposite signs and equal absolute values, so that their algebraic sum is nothing, may be said to *compensate* each other ; and consequently the above statement may be more shortly expressed thus :—*The two transformations which accompany any reversible alteration of a body are mutually compensating.*

Hitherto we have directed our attention to two kinds of transformations exclusively ; we have still, however, to consider transformations of a third kind.

Let us again suppose the given body, whose condition is changed, to be any body whatever ; but let it now be assumed that not merely a single alteration of condition occurs, but a series of alterations which are so arranged that the body finally returns to its original condition, and thus passes through a *cyclical process.*

If the final condition of the body is the same as at the beginning of the cycle, its final disgregation is the same as its original disgregation, and hence, considering the cyclical process as a whole, we may say that no alteration of disgregation is caused by it. But, notwithstanding this, heat may be transformed by it into ergon, or ergon into heat.

Let us suppose that the alterations in the condition of the body which constitute the cyclical process involve changes of volume, in such sort that the body expands at one temperature and

is compressed again at another temperature; then, if the expansion takes place at a higher temperature than the compression, the ergon performed during the expansion will exceed the ergon expended during the compression; and there is thus on the whole a preponderance of ergon performed, and therefore naturally a corresponding quantity of heat is expended. If the cyclical process is gone through the other way, so that the expansion occurs at a lower temperature than the compression, the ergon expended in the compression exceeds that performed during the expansion; and hence the result is a preponderance of ergon expended, and consequently a corresponding quantity of heat must be produced.

Hence, when a body goes through a cyclical process, there is a transformation either of heat into ergon, or of ergon into heat, according to the direction in which the cycle is performed; and the question now arises whether this transformation exists by itself, or whether, as in the simpler cases previously considered, it is accompanied by a further transformation which serves as a compensation.

We will take, in the first place, by way of example, the case in which the expansion occurs at a higher temperature than the compression. In order that the original temperature of the body may be kept up during the expansion, some external body or other, which we may call the body A, must impart to it the heat required to replace the heat expended in ergon during the expansion. When, during the further course of the cyclical process, the temperature is lowered and the body is compressed at this lower temperature, in order that it may retain the same temperature throughout the compression, it must give out, to some other body (which we may call B) of lower temperature, the heat produced from ergon during the compression.

This last quantity of heat, which is produced from ergon during the compression and imparted to the body B, according to what is said above, is not quite as great as that which is withdrawn from the body A during the expansion and expended in the performance of ergon. The excess of the latter quantity of heat over the former quantity is permanently transformed into ergon by the cyclical process. Of the remainder of the heat, however, which is withdrawn from the body A, that portion namely which, though at first converted into ergon is afterwards converted back again from ergon into heat and given up as such to the body B, we may say that it is transferred from the body A of high temperature to the body B of lower temperature.

The final result of the cyclical process is thus twofold: a certain quantity of heat is permanently transformed into ergon, and

another quantity of heat is transferred from a hotter to a colder body.

If the cyclical process had been gone through in the inverse order, the final result would have been that ergon would have been transformed into heat, and that at the same time an additional quantity of heat would have been transferred from a colder to a hotter body.

It will be thus seen that, even in a cyclical process, the transformation of heat into ergon, or of ergon into heat, is not an isolated occurrence, but is connected with another change, namely the transference of heat from a hotter to a colder body, or from a colder to a hotter body; and hence it is natural to regard this transference of heat as a compensation for the transformation which it accompanies.

In order that we may employ a form of expression corresponding to that adopted in considering the previous case, we will speak of the passage of heat from a body of one temperature into a body of another temperature as being likewise a transformation, inasmuch as heat of one temperature is in fact thereby transformed into heat of another temperature; and, further, we will call the passage from a higher to a lower temperature a positive transformation, and that from a lower to a higher temperature a negative transformation. We may then express the result at which we have arrived in reference to the cyclical process as follows:—In such a process a positive and a negative transformation occur simultaneously, namely the negative transformation of heat into ergon, and the positive transformation of heat of higher into heat of lower temperature, or the positive transformation of ergon into heat, and the negative transformation of heat of lower into heat of higher temperature.

Examining the matter more closely, we find that the equivalence-value of the transference of heat can be determined in such a way that the two transformations, which occur simultaneously in every reversible cyclical process, are not only of opposite signs, but are always of equal absolute values, so that in the algebraic sum they exactly counterbalance each other. It is very easy to assign the equivalence-value, determined in accordance with these conditions, of the passage of heat from one temperature to another; it is in fact the value that would be obtained as the resultant value of the double transformation if the heat were to be transformed into ergon at the one temperature, and reproduced from ergon at the other temperature.

If we now consider conjointly the three kinds of transformation that we have been discussing, namely the alteration of disgregation, the transformation of heat into ergon, or *vice versâ*, and, lastly, the transference of heat, we can establish a theorem

which is no longer applicable merely to the changes of condition of a single body, or even to such a series of changes of condition as constitute a cyclical process, but which holds good also for any series whatever of changes of condition that occur in a reversible manner, either of one body or of a number of bodies. This is the theorem known as the Second fundamental Theorem of the Mechanical Theory of Heat, the elucidation of which was the object of the foregoing considerations. It runs as follows :—

In any process, how complicated soever it may be, whereby one or more bodies undergo any reversible alterations whatever, the algebraic sum of all the transformations which take place must be zero.

It will be seen at once that a great degree of similarity obtains between this theorem and the first fundamental theorem of the mechanical theory of heat. According to the first fundamental theorem, heat and ergon are related to each other in such wise that, in order to produce ergon an equal quantity of heat must be expended, and in order to produce heat an equal quantity of ergon must be expended. Production and expenditure can, however, be included under a single conception by counting expenditure as negative production. The foregoing relation may therefore be thus expressed :—*In every process the algebraic sum of the heat and ergon produced is zero* ; and, in exact correspondence with this, the second fundamental theorem asserts that *the algebraic sum of the transformations is zero.*

Consequently, if the first theorem is called the *Theorem of the Equivalence of Heat and Ergon,* the second may be naturally called the *Theorem of the Equivalence of Transformations.*

This second theorem can be represented mathematically by an equation of equal simplicity with that which expresses the first theorem ; and these two equations are the two fundamental equations, whence all further equations which the mechanical theory of heat is capable of yielding must be deduced.

If the equation which expresses the first theorem, even by itself, leads to an extensive series of important conclusions, it will be easily understood that, by combining with it the second equation, the fruitfulness of the theory must be increased still further to a very considerable extent, inasmuch as the second equation is not only capable, like the first, of leading to new conclusions when taken by itself, but from the combination of the two equations additional equations of a different form can be deduced, and these in their turn lead to still further consequences.

A series of important results has in fact already been arrived at by applying the second fundamental theorem. I may mention as examples :—the determination of the volumes of saturated vapours ; the determination of the quantity of vapour which is precipitated when a saturated vapour expands in an envelope

that is impenetrable by heat; and the extensive remodelling which the theory of the steam-engine, and the theory of thermo-dynamic machines in general, has undergone, a change wherein the second fundamental theorem has played at least as important a part as the first.   In like manner I might quote from other departments of physics many additional and not unimportant results which have been arrived at as consequences of this theo-rem ; and without doubt the number of such results will become continually greater when the theorem has been more extensively applied.   The points of connexion between the two theorems, in the investigations that have been carried out by help of the mechanical theory of heat, are so numerous and so intimate that but few of these investigations are intelligible without a know-ledge of the second theorem.

It has been said above that the two fundamental theorems of the mechanical theory of heat are very similar to each other.   I must now, however, direct attention to an essential difference, the existence of which indicates a very remarkable characteristic of all natural processes.

In the foregoing considerations from which we deduced the second fundamental theorem, it was made a condition through-out that all the changes that occurred should be *reversible*—that is, that they should take place in such a way that the reverse changes should be capable of occurring under the same condi-tions.   We must now put to ourselves the question, what results should we arrive at if this condition were abandoned ?

Let us examine, in the first place, the alteration of the dis-gregation of a body, connecting our considerations, as before, with the case of a perfect gas which undergoes a change of volume.

If a gas expands and at the same time overcomes at every instant the greatest possible external pressure that its expansive force enables it to overcome, so that its pressure and the resist-ance are always equal to each other, or at least so nearly equal that the excess of one over the other may be disregarded, then, by the application of the same external force as the gas overcame during its expansion, it can be compressed again to its original volume, all the phenomena taking place during the compression in the inverse direction from what they did during the expansion, but otherwise in the same way.   This kind of expansion of a gas is, accordingly, reversible.

The expansion of a gas may, however, take place in a different manner.   Let us suppose a vessel in which the gas is contained, and let us assume that this vessel is suddenly put into commu-

nication with a second empty vessel ; a portion of the gas will then pass into the empty vessel until the pressure in both vessels has become equal. The gas has then expanded without overcoming any external force ; but we cannot restore it to its former volume without the application of an external force. In this case, therefore, the expansion of the gas has taken place in an unreversible manner.

The final result of the expansion is in both cases so far the same, that the disgregation of the gas has been increased to a certain extent ; but in the one case, where a resistance had to be overcome, heat was transformed into ergon, while in the other case, where there was no resistance to overcome, no ergon was done, and accordingly no heat was transformed into ergon. If, on the other hand, it is required to compress the gas again and so to diminish its disgregation, it is not possible to do this otherwise than in such a way that ergon is transformed into heat. But since the transformation of ergon into heat is a positive transformation, and that of heat into ergon a negative transformation, the above result may be expressed as follows :—A diminution of disgregation, which is a negative transformation, cannot take place without a simultaneous positive transformation ; while it is possible, on the contrary, for an increase of disgregation, which is a positive transformation, to take place without a negative transformation.

Let us now consider the second kind of transformation, or the transformation of heat into ergon, or *vice versâ*, in relation to the same point.

In order that heat may be transformed into ergon, it is necessary, as we have already seen, that either an increase of disgregation should take place, or if this does not occur, as in the case of cyclical processes, a certain further quantity of heat must be transferred from a hotter to a colder body. But since increase of disgregation and passage of heat from a hotter to a colder body are positive transformations, it follows that the negative transformation of heat into work is necessarily connected with a simultaneous positive transformation.

On the other hand, the positive transformation of ergon into heat can quite well take place without any simultaneous negative transformation. When, for example, force is expended in overcoming the resistance of friction, heat is produced, and thus ergon is transformed into heat without its being at all needful that any negative transformation should take part in the process. In like manner, the resistance of the air and the resistance to conduction which an electric current has to overcome in a conductor comport themselves in the same way as the resistance of friction.

Consequently the proposition holds good of the second kind of transformation also, that the negative transformation of heat into ergon cannot occur without a simultaneous positive transformation, but that the positive transformation of ergon into heat can take place without a simultaneous negative transformation.

Finally, we have still to consider the third kind of transformation, or the passage of heat from one temperature to another.

In order that heat may be transferred from a colder to a hotter body, it is a necessity that a positive transformation should form a part of the same process, as indeed we have seen already, in connexion with cyclical processes, that such a transference of heat involves the transformation of ergon into heat. The inverse transference of heat from a hotter to a colder body, on the contrary, can go on entirely by itself, as it does, for example, when heat passes from a hotter to a colder body by radiation or conduction.

Hence in this case also, just as in the two previous ones, the negative transformation cannot occur without a positive transformation ; but the positive transformation can occur without a negative transformation.

When two transformations are equal in magnitude but of opposite signs, we agreed above to say that they *compensate* each other. Accordingly we may enunciate the following theorem in reference to all the three kinds of transformations :—*Negative transformations can take place only when they are compensated, but positive transformations can occur even if uncompensated*; or, shorter still, *Uncompensated transformations can never be anything but positive.*

This peculiar relation is met with in every change that occurs in nature; for the case of an alteration being completely reversible, so that the sum of all the transformations involved in it is exactly zero, is merely the limiting case of an infinite number of possible cases, just as zero itself is the lower limit of all positive magnitudes. When we consider the universe, keeping this relation in mind, we arrive at a very remarkable conclusion.

One hears it often said that in this world everything is a circuit. While in one place and at one time changes take place in one particular direction, in another place and at another time changes go on in the opposite direction ; so that the same conditions constantly recur, and in the long run the state of the world remains unchanged. Consequently, it is said, the world may go on in the same way for ever.

When the first fundamental theorem of the mechanical theory of heat was established, it may probably have been regarded as an important confirmation of this view. Hitherto, when discussing this theorem, we have spoken only of heat and ergon ; but

it must be observed that we may regard the word "heat" as also including light; and the conception of "ergon" is very much more comprehensive still. Chemical action, the effects of electrical and magnetic forces, the production and cessation of motion, whether it be the progressive, rotatory, or vibratory motion of ponderable masses, or whether it be the motion of electricity, may all, so far as they are here considered, be represented as ergon. We are consequently dealing with a theorem that applies to all natural phenomena.

Helmholtz, who at once recognized this general significance of the theorem, and established it clearly and convincingly in his beautiful essay on this subject by applying the theorem to the various branches of physics, gave to the theorem, when thus extended as widely as possible, the name of the *Theorem of the Conservation of Force*, for which it would perhaps be a little better still to say the *Theorem of the Conservation of Energy*.

When the object is to make it express a general fundamental law of the universe, this theorem may be put into some such form as the following:—*One form of Energy can be transformed into another form of Energy, but the quantity of Energy is thereby never diminished; on the contrary, the total amount of Energy existing in the universe remains just as constant as the total amount of Matter in the universe.*

Notwithstanding that the truth of this theorem is beyond a doubt, and that it expresses the unchangeableness of the universe in a certain very important respect, we should yet be going too far were we to assume that it affords a confirmation of the view according to which the whole condition of the universe is represented as unchangeable, and all involved in never-ending cycles. The second fundamental theorem of the mechanical theory of heat contradicts this view most distinctly.

As was said above, the common rule holds good for all the endlessly manifold changes which go on in the world, that transformations in opposite directions do not necessarily occur in equal numbers, but that the difference can only be on one determinate side, namely, so that the positive transformations preponderate over the negative. Hence it follows that the condition of the universe must gradually change more and more in a certain particular direction.

The ergon which the forces of nature are capable of performing, and which is contained in the existing motions of the bodies which make up the system of the universe, will be gradually converted more and more into heat. The heat, inasmuch as it always tends to pass from hotter to colder bodies, and so to equalize existing differences of temperature, will gradually acquire a more and more uniform distribution, and a certain equi-

librium will be attained even between the radiant heat existing in the æther and the heat existing in material bodies. Lastly, in relation to their molecular arrangement, material bodies will get nearer to a certain condition in which, regard being had to the existing temperature, the total disgregation is the greatest possible.

I have endeavoured to express the whole of this process by means of one simple theorem, whereby the condition towards which the universe is gradually approaching is distinctly characterized. I have formed a magnitude which expresses the same thing in relation to transformations that energy does in relation to heat and ergon—that is, a magnitude which represents the sum of all the transformations which must have taken place in order to bring any body or system of bodies into its present condition. I have called this magnitude *Entropy*. Now in all cases in which the positive transformations exceed the negative an increase of entropy occurs. Hence we must conclude that in all the phenomena of nature the total entropy must be ever on the increase and can never decrease ; and we thus get as a short expression for the process of transformation which is everywhere unceasingly going on the following theorem :—

The entropy of the universe tends towards a maximum.

The more the universe approaches this limiting condition in which the entropy is a maximum, the more do the occasions of further changes diminish ; and supposing this condition to be at last completely attained, no further change could evermore take place, and the universe would be in a state of unchanging death.

Albeit the present condition of the universe is still very far removed from this limiting condition, and the approach to it is so slow that all such periods as we speak of as historical are but a very short span in comparison with the immeasurable periods that the universe requires for comparatively very slight modifications, it yet remains an important result that a law of nature should have been discovered which allows us to conclude with certainty that everything in the universe does not occur in cycles, but that it changes its condition continually in a certain direction, and thus tends towards a limiting condition.

XLVIII. *Example of the Application of a Graphical Method to the Problem of Rectilinear Motion in a Homogeneous Resisting Medium.* By C. W. MERRIFIELD, *F.R.S.*[*]

THE equation of the motion is in general

$$\frac{dv}{dt} = \phi(v),$$

which, being integrated, leads to

$$t = \mathrm{F}(v) - \mathrm{F}(v_0) ;$$

and this equation has to be solved for v, which is only possible in a few very limited cases. In all other cases it is necessary to have recourse to very tedious arithmetical applications of the method of quadratures, or to graphical methods. The object of this paper is to give an example of the latter.

In the case which actually occurred, the problem presented itself under the form

$$\frac{dv}{dt} = \pm g - kv^3,$$

k being a known coefficient of resistance. The process adopted was to tabulate the functions

$$\frac{1}{g} - \frac{1}{g + kv^3} \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

and

$$\frac{1}{g - kv^3} - \frac{1}{g} \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

from $v = 0$ (that is to say, taking the point of rest for origin) for equidistant values of v. The tabulated values of each were then laid off on a sheet of squares as ordinates of a curve, which was then integrated, so as to give a new curve, by the following rule. The tabulated ordinates being $a, b, c, \ldots$ &c., those of the new curve will be

$$0,$$
$$\tfrac{1}{2} a + \tfrac{1}{2} b,$$
$$\tfrac{1}{2} a + b + \tfrac{1}{2} c,$$
$$\tfrac{1}{2} a + b + c + \tfrac{1}{2} d, \ \&c.$$

These are very quickly obtained by measuring with a strip of paper.

The integrated curve due to the motion *in vacuo* is easily seen to be a right line making an angle $= \tan^{-1} \dfrac{1}{g}$ with the axis of v.

The scale of the ordinates of this line, and of the two curves, must then be made to correspond, and also to fall within convenient limits. The ordinates of the curves must then be set off as additive or subtractive to those of the vacuum-line.

We have hitherto used v as the independent variable. We have now to make t the independent variable in order to integrate $\dfrac{ds}{dt} = v$.

In the accompanying diagram, let O, at the left-hand lower corner of the sheet of squares, represent the origin, point of rest, or highest point, in the case of a projectile thrown upwards, and let v be reckoned horizontally towards the right. Then we may

Spaces (curves OU_0, OU_1, OU_2).

O (point of rest).   Velocities (curves OW_0, OW_1, OW_2).   V
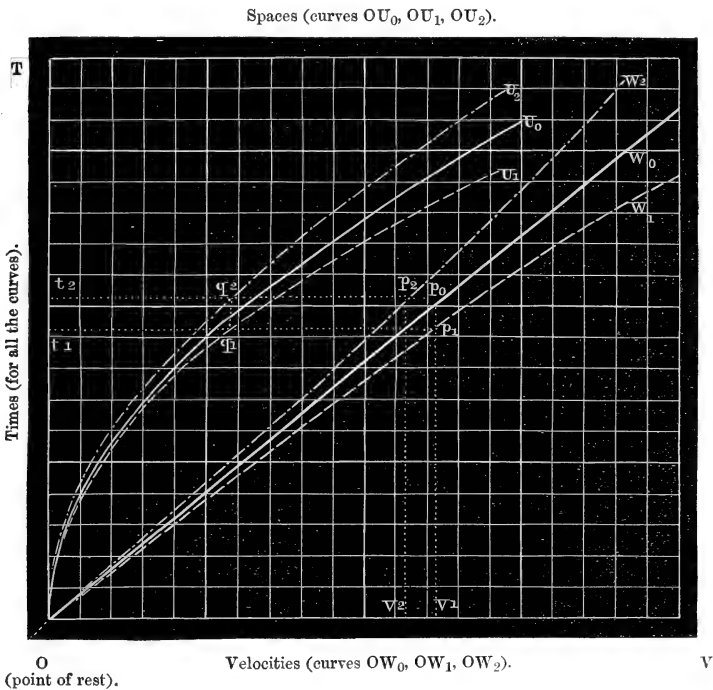
call the line OW_0 the vacuum-line, the curve OW_1 that belonging to the rise, and OW_2 that belonging to the fall.

We must now take the axis of t (the left-hand side of the sheet) as the line of abscissæ, and we must integrate all the three curves from O upwards, taking v as the ordinate, instead of, as before, the abscissa. We use the same rule as before, dividing any selected value of t into a number of equidistant parts, to suit

practical convenience. The resulting curves we will call OU_0, OU_1, and OU_2 respectively.

The ordinates of these new curves will be the spaces traversed.

Our problem is now solved. Along the left-hand side of our sheet we have t as the current abscissa or equidistant variable, and we have the ordinates of the curves

$$OW_0, \ OW_1, \ OW_2 \ \text{for the velocities,}$$

$$OU_0, \ OU_1, \ OU_2 \ \text{for the spaces.}$$

It is to be observed that the curve OW_1, giving the rising velocity, corresponds to $\dfrac{1}{g} - \dfrac{1}{g + kv^3}$, and the curve OW_2, the falling velocity, to

$$\frac{1}{g - kv^3} - \frac{1}{g}.$$

As an illustration of the use of the diagram, let us suppose that a body is projected upwards with a given velocity, and that we require to compare its total time of flight with what it would have been *in vacuo.*

Set off v_1 along OV. Draw the ordinate $v_1 p_1$ to meet the curve OW_1. Draw $p_1 q_1$ to meet the curve OU_1 parallel to OV. Now the space of fall has to be equated to the space of rise. Hence we draw, to meet the curve OU_2 in q_2, a right line $q_1 q_2$ parallel to OT. The distance of q_2 from OV gives the time; and by drawing $q_2 p_2$ to meet OW_2 in p_2 we get the velocity at the lowest point. We thus get the times, spaces, and velocities in the resisting medium, and we have only to perform similar operations on the vacuum-lines to complete the comparison. In fact if p_0 be the point corresponding to v on the curve OW_0, the difference of time in the resisting medium is given at once by

$$2v_1 p_0 - (v_1 p_1 + v_2 p_2) \, ;$$

and it is easily seen that we may obtain, by simple constructions, any other such comparison as we may desire.

Besides being convenient for the purpose of comparison, the curves for vacuum enable us to verify our units of scale. This is a point at which error is very likely to creep in.

It has been suggested to me by some friends, to whom I have shown this, that it might be desirable to publish it, as an example of the value of graphical methods, and also as the graphical solution of a question to which considerable interest now attaches, with reference to the theory of projectiles. The chief point of novelty is the change of the independent variable by the inversion of the diagram.

The accompanying diagram is not done to scale, but is merely drawn to exemplify the process. In actual work I use a sheet 25 × 25 inches, divided into 100 × 100 squares, each of a quarter of an inch, with every fifth line strong, to assist in counting.

Royal School of Naval Architecture,
April 30, 1868.

XLIX. *On a New Thermometer for measuring Temperatures above the Boiling-point of Mercury.* By M. Berthelot*.

[With a Plate.]

PROBABLY every chemist and physicist has had occasion to feel the want of a thermometer capable of measuring high temperatures, of portable size, and sufficiently delicate in its indications. In organic chemistry especially, and in the course of fractional distillation (an operation of frequent occurrence), this want is very generally experienced. Up to 330° or 350° the mercurial thermometer answers every requirement—although as these high temperatures are approached its indications require correction to the extent of 15° or 20°, since the height of the column outside the distilling apparatus has then to be taken into consideration. But beyond this point we possess no thermometer capable of similar indications.

In certain cases only are we able to measure elevated temperatures with anything like precision. The air-thermometer, especially with the latest modifications which M. Regnault and M. H. Deville have given to it, certainly allows of such measurements; but the apparatus occupies considerable space, 300 to 400 cubic centims. at least—a circumstance which limits its use to the determination of the temperatures of large volumes, and consequently deprives it of all its sensitiveness. On the other hand, the air-thermometer, as it has been hitherto employed, never directly indicates the true temperature; this is only derived from a long calculation in which numerous corrections occur.

A sensitive thermometer of a size small enough to allow of its use in operations conducted in retorts or flasks, and indicating directly and without correction temperatures beyond 350°, was therefore a desideratum.

Such an instrument I believe I have succeeded in constructing. The thermometer which I am about to describe allows of measurements up to 500°, and may even be employed up to the temperature at which a glass retort commences to fuse. It is

* Translated from the *Annales de Chimie et de Physique*, February 1868, by Mr. T. E. Thorpe.

equally applicable, and without limit, to the measurement of very low temperatures, even below the freezing-point of mercury. We might construct a thermometer on the same principle capable of use up to 1200° or 1500° by employing a reservoir of porcelain instead of glass.

I will describe only the thermometer with the glass reservoir adapted for measurements up to 500°. In the first place I will give a description of the apparatus, indicate the method of its graduation, discuss the theory of it, and, lastly, specify some of the applications which I have already made of it.

I. *Description of the Thermometer.*

The new thermometer (Plate VI. fig. 1) consists of an air-reservoir, a capillary stem, a reservoir filled with mercury, a graduated scale, and a firm support for the whole.

(1) The air-reservoir (B) is made of hard glass, of cylindrical shape, 40 millims. in length and 12 millims. in diameter. Its walls are moderately thin, and its internal capacity is about 4 cubic centims. These dimensions have been adopted in order to allow of the introduction of the thermometer into a tubulated retort of 125 cubic centims. capacity, but they may be enlarged at will if larger vessels are to be used.

The neck of the reservoir is fused to a capillary stem.

(2) The stem *t t h h l l l l m m n n* is nearly 1200 millims. in length, and its internal diameter is about one-fifth of a millimetre. If reservoirs of greater capacity are employed, the bore of the capillary tube may be augmented to half a millimetre, or even beyond this.

In every case the tube ought to be carefully calibrated by means of a small column of mercury, in order to see if its bore be perfectly uniform.

The tube thus verified is fused to the neck of the reservoir B. It has the form and disposition represented in fig. 1 ; the vertical portion is about 730 millims. in length, and is terminated by a large glass bulb, Q, with a cylindrical opening at the upper end. The stem *t t h h l l l l m m n n* ought to be of a single piece and without any intermediate joining. This is an essential point, since every joining produces a cavity, which interferes greatly with the uniform capillarity.

Another necessary precaution is to thoroughly dry both the capillary tube and the air-reservoir B. This is done immediately after sealing the stem and air-reservoir together, and when the lower end of the latter is still open and drawn out to a point. This open point is placed in communication with an aspirator through which air is continually drawn, whilst the bulb Q and the capillary tube are strongly heated, by means of a lamp, throughout

their entire length, the air being of course dried before it enters the apparatus. The vapour of water, which otherwise obstinately adheres to the glass in the capillary tube, is thus expelled. When the entire length of the tube has been thus heated, the open end of the air-reservoir B is closed and the whole allowed to cool.

(3) The reservoir of mercury is contained in the bulb Q; this is fused to the end of the capillary stem, its other extremity being shaped like the neck of a bottle. In order to avoid the introduction of dust, this orifice is closed by a loosely fitting cork, just sufficient to permit of the transmission of the atmospheric pressure when the instrument is in use. The method of filling this reservoir will be described presently.

(4) The flat graduated scale, R R, is made of wood, and is fixed along the entire length of the vertical portion *l l l l* of the stem; it is consequently about 750 millims. in length. This scale is held by the two small metallic clips *p, p*, which may be tightened or loosened at pleasure by means of screws, so that it may slide along the length of the stem *l l l l*. The scale is further supported by the metallic branch A A, adapted to the foot of the instrument.

This scale is divided into two distinct systems of graduation; the one to the left of the capillary tube is in millimetres, the divisions commencing from the top; the other, to the right, is divided into thermometric degrees, made empirically and by means of certain fixed points which will be indicated presently.

(5) The support. The thermometer is held by a firm and heavy support. This support consists—

1. Of a grooved shoulder, C C, upon which the horizontal portion of the stem *h h* rests.

2. At right angles to this shoulder and near one extremity is soldered the metallic rod T T, in diameter about 5 or 6 millims. This rod carries the horizontal branch A A, which has at its other extremity a vertical slit to admit the wooden scale, R R.

3. The rod itself is firmly fixed to the foot P P, sufficiently heavy to give the requisite degree of stability to the whole apparatus.

II. *Graduation of the Thermometer.*

This may be divided into three operations: (1) filling the instrument; (2) determination of the fixed points; (3) graduation of the scale.

1. *Filling the Instrument.*

In order to fill the thermometer, a sufficient quantity of pure dry mercury is poured into the bulb Q so as to half fill it; a partial vacuum is then made in the bulb by means of an air-pump, the exhaustion being continued until the pressure is re-

duced to about 20 or 25 centims. of mercury. The air as it leaves the apparatus passes through the mercury. On reestablishing the atmospheric pressure the mercury is driven into the capillary tube.

In order to ascertain if a sufficient vacuum has been made, the air-reservoir B is plunged successively into a bath of melting ice and into water at the ordinary temperature. The diminution in internal pressure is thus determined by the recession of the mercurial column contained in the capillary tube. The number of millimetres on the scale through which the mercury column passes ought to be nearly equal to that which expresses the temperature of the water employed—that is, if the thermometer is intended to indicate temperatures up to 500°. If the exhaustion has not been sufficient, this number will be too large; it will be therefore necessary to continue the exhaustion. On the other hand, if the proper degree of exhaustion has been passed—for example, if the pressure has been reduced to 10 or 12 centims., the bulb must be completely emptied of the mercury and the operation recommenced.

The bulb Q ought to be of considerable diameter, in order that the level of the mercury contained within it may only be inappreciably affected by the variations in the height of the mercurial column in the capillary tube. The employment of a considerable quantity of mercury has also the advantage of rendering the mercury in the capillary tube more susceptible of motion. By slightly tapping the instrument the meniscus readily assumes its normal form, and the indications are rendered perfectly regular.

2. *Determination of the Fixed Points.*

In order to graduate the instrument, I have adopted the following fixed points :—

<div align="center">

The melting-point of ice . . .	$\overset{\text{c}}{0}$	
The boiling-point of water . .	100	
,, ,, mercury .	350	
,, ,, sulphur .	440	

</div>

These four points ought to be determined upon the same **day**, and within an interval of time so short that the barometric pressure does not undergo any appreciable variation; by this I understand a variation of a millimetre. The zero-point is determined by plunging the air-reservoir B, together with a few centimetres of the capillary tube *t t*, into melting ice, with the usual precautions. The stem *l l l l* must be carefully fixed in a vertical position. After a few minutes, and when the mercury column remains stationary in the portion of the tube marked *l l l l* in the figure, the wooden scale is slightly tapped below the

support A A, in order to bring the column to a definite state of equilibrium. When all oscillation has ceased, the number of millimetres and fractions of millimetres corresponding to the height is read off upon the graduated scale. This is the zero-point under the barometric pressure at the time of the experiment.

The point 100 is then similarly determined by placing the reservoir B in a flask in which distilled water is made to boil.

The point 440 is next determined. The air-reservoir B is placed in a tubulated retort containing sulphur, which has previously been fused and allowed to solidify ; the tubulure is closed by a cork pierced to admit the stem *t t*, and cut down the middle so as to fit closely round it. The retort is firmly fixed upon a stand and the air-reservoir placed within it, the capillary stem being held in the centre of the tubulure. The two halves of the cork are then carefully pushed down between the stem and the tubulure in such a manner as to close the opening. The beak of the retort is next placed in a receiver, and the sulphur heated by a large gas-lamp until it perfectly boils and distils in a continuous stream. The air-reservoir ought to be fixed partly in the boiling sulphur and partly in its vapour (see fig. 1).

The point 350 is then determined by means of boiling mercury. This operation is performed exactly as in the determination of the boiling-point of sulphur, but with the following extra precautions. The air-reservoir B dips partly under the surface of the mercury : it must of course be firmly fixed, in order that it may not be jerked out of position by the upward pressure of the metal. The tubulure of the retort must also be more carefully closed, to avoid the introduction of mercurial fumes into the atmosphere of the laboratory. The upper surface of the cork is therefore to be covered with a luting of pipeclay. Above all, the ebullition must be very carefully conducted,—a needless caution, perhaps, to all who have had occasion to distil mercury.

After this operation it is absolutely necessary to verify the capacity of the air-reservoir B, in order to ascertain if it has undergone any variation by exposure to the temperatures of 350° and 440°. This is easily done by redetermining the zero- and 100°-points : the variation ought to be *nil*, or very slight. If, however, their position has appreciably changed, it will be necessary to repeat the experiments.

The four fixed points 0, 100, 350, 440 have thus been determined. It may appear at first sight that these points answer only to a certain atmospheric pressure, since the height of the mercury in our instrument will evidently be affected by variations in atmospheric pressure in the same way as the barometer. But it will easily be seen that these oscillations do not affect the length of the spaces between the fixed points when

taken two by two*. It suffices, therefore, to note exactly the length of these interspaces, once and for all, in the first experiment; so that, by taking one of the four fixed points and redetermining its position immediately before using the instrument, the position of the remaining points may be ascertained. When the instrument is about to be used, one of the points, the zero, for example, or, better still, the 100°-point, is redetermined, and by relaxing the screws *p p*, the scale is moved along the stem *l l l l* until the fixed point marked on the scale exactly corresponds to the position of the mercurial column. The tube is then once more fixed to the scale by means of the screws.

3. *Graduation of the Scale.*

The most exact method of graduating the instrument consists in jotting upon curve-paper the temperatures taken for fixed points, the length of the spaces being expressed in millimetres; these points are then connected by a curve after the well-known method. The curve at one end is prolonged to $+500°$, and at the other to $-100°$. The abscissæ will then represent the spaces on the scale expressed in millimetres, and the ordinates the temperatures. The latter are transferred to the graduated scale and engraved to the right of the tube *l l l l*, parallel to the millimetre-divisions.

When the capillary tube is of uniform calibre, the length of each degree diminishes very slowly with the increment of temperature. The variation becomes less when the bore of the capillary tube changes. This may even accidentally produce such a compensatory effect that the length of each degree remains constant; in fact I possess such an instrument.

But the above method of graduation may be considerably simplified when the amount of error to which the instrument is necessarily subject (reaching $2°$ or $3°$ at high temperatures) and the fact that it is specially adapted for temperatures ranging between $300°$ and $500°$ are taken into account. In fact it is sufficient to divide the space between $350°$ and $440°$ into ninety equal parts; each of these divisions represents consequently a degree of temperature. This graduation is extended on the one hand to $300°$, and on the other to $500°$. Between these limits the graduation obtained in this manner agrees sufficiently well with that resulting from the curve deduced from the fixed points; the differences do not exceed the experimental errors.

When the thermometer is graduated according to this method, it is sufficient to mark the $0°$ and $100°$ points without dividing the intermediate space into degrees; these points are intended to

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* Provided, of course, that the capillarity of the tube be perfectly uniform.

serve as starting-points, by which the graduation may be from time to time adjusted.

If one wished to extend the graduation below the zero-point down to $-100°$, it would be necessary to fix upon some other determinate point, situated as low as possible; we should thus possess a far more accurate instrument than the alcohol-thermometer generally employed for low temperatures.

An instrument constructed in the foregoing manner gives, above 300°, indications at least as exact as those of a mercurial thermometer, especially if one considers the amount of correction required by the latter if a considerable portion of the column happens to be unimmersed in the heated space. The errors due to the different expansions of different kinds of glass are equally great in the two instruments. M. Regnault's experiments have shown that even in the best-constructed mercurial thermometers the error produced by this expansion may amount to 5° or 6° at temperatures above 300°.

The indications of the new thermometer present another advantage, namely that they correspond to those of the air-thermometer; at 350° the indications of the latter instrument differ from those of the mercurial thermometer by 10° at least.

The new thermometer is especially useful for temperatures beyond 330°; for the greater number of mercurial thermometers disagree among themselves above that point. When properly constructed, its indications are seldom more than 2° or 3° in error, even at a temperature of 500°.

III. *Theory of the Instrument.*

The trustworthiness of the instrument depends upon two fundamental conditions, namely, the empirical construction of a curve of temperatures by means of fixed points experimentally determined, and the relatively very minute quantity of air contained in the capillary portion of the instrument as compared with the amount of air in the cylindrical reservoir.

In fact the new thermometer may practically be regarded as a reservoir of air of invariable capacity. In such a reservoir the variations in the pressure are proportional to the variations in the temperature. Let V_0 be the volume of the gas at 0° and under an initial pressure H_0. If, now, the temperature is t, the pressure becomes $H_0 + h$, and we have

$$V_0 = V_0(1 + \alpha t)\, \frac{H_0}{H_0 + h},$$

and then

$$1 + \frac{h}{H_0} = 1 + \alpha t;$$

that is,

$$\frac{h}{H_0} = \alpha t,$$

which is the relation signified.

If this capacity were indeed constant, it would be simply necessary to trace by the side of the scale of pressures a scale of temperatures in which the divisions were proportional to those of the pressures. Strictly speaking, however, the condition which determined this relation is not exactly fulfilled in the new thermometer, and for the following reasons :—(1) From the expansion of the glass envelope ; and (2) from the expulsion of a portion of the air contained in the reservoir, which impinges upon the mercury in the capillary tube. But if the dimensions given below are observed, it will easily be seen that this theoretical condition is but slightly altered in practice; the very small divergence renders the accurate construction of the instrument still perfectly possible.

In the first place, we will calculate the possible amount of variation in the capacity of the envelope.

Admitting $\frac{1}{37000}$ for the coefficient of cubical expansion of glass, then from 0° to 500° the capacity of the reservoir will increase by $\frac{500}{37000}$, or by $\frac{1}{74}$. It results, therefore, that the length of a degree on the instrument slightly diminishes from 0° to 500°, being, of course, least at the latter point.

It is needless to calculate the amount of this diminution ; it is sufficient to remark that any objection to our method of graduation, arising from the fact of the gradually increasing capacity of the glass envelope, is nullified when it is considered that this graduation is the result of direct experiment, and is obtained by means of certain empirically fixed points.

We will now consider the effect due to the small portion of air expelled from the reservoir. It will be seen, from the dimensions adopted, that the capacity of the cylindrical reservoir is about 4 cubic centims., and also that the air at zero occupies some 500 to 550 millims. in length of the capillary tube. At 500° this air will occupy about double the length. Let us calculate the increase in volume under the extreme condition, that is, at 500°. Supposing the tube to be $\frac{1}{5}$ of a millimetre in internal diameter, then the capacity of 1 metre in length of this tubing is equal to $\pi \frac{1}{10^2} 1000$ cubic millims., or about 31 cubic millims.

Now this volume represents only the $\frac{1}{130}$ part of the capacity of the reservoir. But the weight of this air represents a much larger fraction of the weight of the air contained in the reser-

voir. In fact the air of the reservoir at 500° is two and a half times less dense than that in the capillary tube possessing the temperature of the surrounding space. The weight of the air contained in the reservoir diminishes, therefore,—

1. By the amount of air contained in the 500 millims. of capillary tube originally filled with mercury at zero, but now at 500° filled with air; this amount is equal to about the $\frac{1}{100}$ part of that contained in the reservoir at 500°.

2. By the difference in the quantity of air contained in the anterior portion of the tube originally at zero, but now at 500°. The pressure, and consequently the condensation of this air, being now tripled, and the length of the one portion of the tube being nearly equal to that of the other (that in which the mercury has been replaced by air), it will be seen that the increment in the amount of air contained in the first portion of the tube is very nearly equivalent to two-thirds of the quantity replacing the mercury in the second portion of the same tube.

The above quantities taken together represent a total diminution of one-sixtieth in the amount of air contained in the reservoir, resulting from the increased temperature.

This diminution will evidently vary with the capillarity of the tube. The foregoing calculations are made for a tube $\frac{1}{5}$ of a millim. in internal diameter. In a tube $\frac{1}{10}$ of a millim. in diameter it would amount only to $\frac{1}{240}$; whilst if the bore were $\frac{1}{2}$ a millim. it would be increased to $\frac{1}{10}$.

We will now trace the consequences of this variation in the amount of air contained in the reservoir. In the first place, it produces another source of diminution in the length of each degree, in addition to that caused by the expansion of the glass envelope. But, after all, this is only a theoretical error, since the length of the degrees is empirically determined by a curve and by means of certain fixed points.

Still the expulsion of a small quantity of air from the reservoir gives rise, theoretically speaking, to a more considerable source of error, although, as we shall show, it may practically be disregarded. This source of error arises from the ordinary variations in atmospheric temperature.

In the different experiments the air contained in the capillary portion does not invariably possess the same temperature, and consequently its volume changes independently of the variations caused by the temperature of the space in which the reservoir is placed. Then in what does our instrument differ from an ordinary air-thermometer?

In the latter instrument, the air it contains is divided into two portions, each of considerable volume; the temperature of the portion beyond the reservoir must therefore be determined

with the greatest accuracy. But it is not thus in the new thermometer, on account of the relatively minute quantity of air contained in the capillary portion. In fact, as we have seen, the quantity of air contained in the reservoir at 500° is less than the quantity contained at zero by about $\frac{1}{60}$, on the supposition that the capillary tube possesses an internal diameter of $\frac{1}{5}$ of a millim. The total quantity of air in the capillary tube is even slightly increased; since this tube already contains air at 0°, the entire quantity at 500° is increased to about $\frac{1}{50}$ part of the quantity contained in the reservoir.

It is the temperature of this portion of air in the capillary tube that varies with the surrounding temperature, and consequently its volume changes and exercises a certain degree of influence on the position of the mercurial column.

To calculate the magnitude of this source of error, we will suppose the instrument to be graduated to the temperature of 15°, and the circumambient temperature to vary between the limits of 0° and 30°, that is, 15° in either direction. Now, since a determinate volume of air varies $\frac{11}{3000}$ of its bulk for each degree of temperature, it follows that the extreme variation will amount to $\dfrac{11 \times 15}{3000}$, or about $\frac{1}{20}$ of the volume contained in the capillary portion. But this last represents, even in the extreme case, only $\frac{1}{50}$ of the quantity of air contained in the reservoir. Therefore the variation due to the influence of the circumambient temperature is equivalent to a change of a $\frac{1}{1000}$ part at most; and this represents on the instrument not more than 0·3 of a degree; it may therefore be neglected. And even supposing the capillary tube of the instrument to be $\frac{1}{2}$ a millim. in diameter, the variation would only amount to $\frac{1}{200}$ of the volume of the air in the reservoir, a quantity which scarcely exceeds the limit of experimental error.

IV. *Applications.*

This instrument, when well-constructed and its capillary tube properly calibrated, indicates high temperatures within 2° or 3° of the truth; within these limits I believe it to possess considerable utility.

The new thermometer is especially adapted to the determination of temperatures lying between 330° and 500°. It is used exactly as a mercurial thermometer, except that the scale requires to be readjusted at the commencement of the experiment by redetermining either the zero- or the 100°-point.

I have employed this thermometer in the fractional distillation of coal-tar at temperatures between 330° and 450° with great success. Tubulated retorts may be used in the ordinary way,

the thermometer being fixed in the tubulure by a divided cork in the manner above described. The heat may be urged until the retort commences to soften.

In the distillation of coal-tar I have observed that towards 450° this substance intumesces, slowly evolves hydrogen, and is changed into carbonaceous matter. At this temperature the greater number of organic compounds, even of the most stable constitution, commence to decompose.

The boiling-points of bodies but slightly volatile may be in this way easily determined. I have ascertained, for example, that retene, $C^{36} H^{18}$, boils at 390°, and that perchlorinated naphthalene, $C^{20} Cl^8$ (prepared by means of antimony chloride), boils at 403°. I have also found that the boiling-point of sulphur remains constant during the entire process of its distillation.

The thermometer as above described was made by M. Alvergniat, Passage Sorbonne, with his well-known skill. Its form is that of a thermometer to be used in fractional distillation. But it is clear that the reservoir B and the anterior portions of the capillary tube may possess any direction required by the nature of the operation in which the instrument is intended to be employed.

L. *On the Periodic Change of Climate caused by the Moon. By* Charles V. Zenger, *Professor of Natural Philosophy at the Polytechnic School at Prague**.

IT is now generally admitted by meteorologists that the influence of the moon on atmospheric pressure and temperature is scarcely appreciable, if computed by means of short periods, as those of its synodical revolutions. The rapid motion of the nodes and of the apsides produces a constant and periodic change of positions from one synodical revolution to another; yet no reference to it is made in researches instituted for the purpose of accounting for the lunar influence on climate. The investigations of MM. Schübler, Kreil, and Buys de Ballot on that interesting object, though partially based on a large series of observations, have failed to ascertain the lunar influence in question.

Yet the object seems to merit that new attempts should be made, seeking a solution in other ways and by other means than formerly were used. Success seems to me to depend on finding out the true period of lunar influence; and that is only possible by computing a large series of observations carefully made at short intervals with apparatus well adjusted and placed at a constant height above the ground. I therefore resolved to calculate the observations of the Meteorological Observatory of Prague, made from 1840 till 1866, hourly, by means of self-registering apparatus.

* Communicated by the Author.

TABLE I.—Temperature at Prague, 1840–66.

Year.	January to March.	April to June.	July to September.	October to December.	Winter.	Summer.	Average.
	R.						
1840.	−2·11	34·67	43·64	6·37	4·26	78·81	6·881
1841.	−2·84	37·96	45·20	18·28	15·44	83 15	8·217
1842.	−2·51	34·56	50·24	9·42	6·91	84·80	7·642
1843.	+6·21	31·12	42·08	15·08	21·29	73·21	7·875
1844.	+5·28	32·56	38·21	10·01	10·54	70·77	6·776
1845.	−6·99	32·31	41·46	14·90	7·91	73·77	6·807
1846.	+8·09	35·36	47·12	9·08	17·17	82·48	8 304
1847.	+2·04	31·16	41·97	9·44	11·48	73 13	7·051
1848.	−0·27	36·64	42·11	11·40	11·13	78·75	7·490
1849.	+3·16	33·12	40·23	8·02	11·18	73·35	7·044
1850.	−0·97	33·24	41·52	12·10	11·13	74·76	7·158
1851.	+2·73	31·52	40·03	11·24	13·97	71·55	7·127
1852.	+5·06	31·74	45·75	16·18	21·24	77·49	8·227
1853.	−1·22	29·31	43·82	5·61	4·39	73·13	6·460
1854.	+2·48	32·39	42·30	11·43	13·91	74·69	7·384
1855.	−5·25	31·18	42 22	8·51	3·27	73·41	6·389
1856.	+3·22	34·84	41·40	9·33	12·55	76·24	7·399
1857.	−1·63	33·86	45·84	13·29	11·66	79·70	7·614
1858.	−4·92	33·23	44·31	6·77	1·86	77·54	6·616
1859.	+8·89	33·95	47·89	9·53	18·42	81·84	8·355
1860.	+2·10	34·33	40·69	7·36	9·46	75·01	7·039
1861.	+2·75	31·62	45·42	12·64	15·39	77·02	7·702
1862.	+3·51	37·05	42·44	14·03	17·54	79·48	8·085
1863.	+9·35	34·01	44·95	16·16	25·51	78·95	8·705
1864.	+5·17	29·32	40·68	5·14	10·31	70·00	6·692
1865.	−4·97	36·28	46·77	13·28	8·31	83·05	7·614
1866.	+9·60	35·34	43·65	12·26	21·86	78·99	8·404

TABLE II.—Atmospheric Pressure at Prague, 1848–66.

Year.	900‴+.				1800‴+.	
	January to March.	April to June.	July to September.	October to December.	Winter.	Summer.
1848.	80·29	74·90	76·64	84·93	165·23	151·54
1849.	91·36	85·41	89·18	88·95	180·31	174·59
1850.	90·09	86·83	89·71	87·75	177·84	176·54
1851.	89·62	87·88	88·78	90·27	179·89	176·66
1852.	89·52	87·04	87·52	86·76	176·29	174·56
1853.	82·56	83·79	87·99	89·35	171·91	171·78
1854.	90·61	85·79	89·56	83·79	174·40	175·35
1855.	85·29	87·90	90·98	88·94	173·23	178·87
1856.	90·29	86·21	88·52	91·39	181·68	174·73
1857.	91·05	87·89	90·61	96·97	188·02	179·50
1858.	93·91	88·72	88·64	90·57	184·48	177·36
1859.	92·16	84·50	89·62	88·41	180·57	174·12
1860.	85·06	85·91	86 76	87·61	172·67	172·67
1861.	89·49	88·08	87·84	91·89	181·39	175·19
1862.	87·41	87·40	88·40	89·76	177·17	175·81
1863.	90·23	87·53	89 14	91·11	181·34	176·67
1864.	89·97	88·91	90·12	91·37	181·34	178 03
1865.	84·75	92·94	91·91	91·89	176·64	184·00
1866.	86·34	88·94	86·95	89·77	176·11	175·89

The Tables (I. & II.) of monthly mean temperatures and atmospheric pressures during that period of 27 years show that the highest annual temperature was in 1863 8°·705 R., the lowest in 1855 6°·389, the average of the extremes being 7°·599 R. The years showing nearly the mean annual temperature of 7°·599 were the following :—

	Average.	Difference.	Period.
1842.	7·642	+0 043	7 years.
1848.	7·490	−0·109	10 ,,
1857.	7·614	+0·015	9 ,,
1865.	7·614	+0·015	

The mean period is 8·7 years; during that time the annual temperature repeatedly reaches twice the average of the extremes; also the extremes in 1855 and 1863 show a period of 9 years.

The periodic change of the lunar perigee (8 years 310·5 days) and of the inclination of the moon's orbit to the ecliptic (9 years 109·5 days) nearly coincides with the periodic change of annual temperatures above mentioned. If the radiation of heat reflected on the earth by the moon is perceptible, the amount of heat received by the earth's surface must depend on the inclination of the lunar orbit to the ecliptic, and on the distance of the moon from the earth.

Suppose S to be the sun, M E the projection of the lunar orbit in its maximum of inclination, *m* E in its minimum, *μ* E in the mean position, S E the projection of the ecliptic, it is evident that the radiant heat will be reflected by the moon in higher quantity in the position *m* E than in the mean position *μ* E, and in the position (maximum) M E. Hence we must suppose the radiant heat will be sent to the earth on a larger scale during a period of 4 years 8 months nearly, when the moon, from the mean position of its orbit, approaches to the minimum of inclination, than during the same time when she is approaching the maximum of inclination.
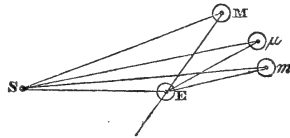
The following Table contains the relative position of the node ☊☾ to the inclination of the orbit, and the average of annual temperatures during the periods of 4 years 8 months :—

Year.	Months.	☊ ☾.	Inclination.	Period.	Average of annual temperature.	Difference.
1843.	7·25	270°	Mean.	From mean to min.	6·949	
1848.	3·00	180	Minimum.	„ min. to mean.	7·881	
1852.	11·00	90	Mean.	„ mean to max.	6·922	+0·959 R.
1857.	6·70	0	Maximum.	„ max. to mean.	7·178	
1862.	2·60	270	Mean.	„ mean to min.	8·402	+1·224 „
1866.	9·80	180	Minimum.			

It results that during the period of a whole revolution of the nodes from 1848–66 the average of annual temperatures is larger for 1848–52 (from minimum to mean inclination) than in the following period, 1852–57 (from mean to maximum); the same follows from the periods 1862–66 (from mean to minimum) and the preceding 1857–62 (maximum to mean).

			Average.	Difference.
Taking the period	1843–48.	Mean to min.	6·949	+0·932
„ „	1848–52.	Min. to mean.	7·881	
		Mean	7·415	
„ „	1852–57.	Mean to max.	6·922	+0·256
„ „	1857–62.	Max. to mean.	7·178	
		Mean	7·050	

we find a difference between the averages of annual temperature during the periods of minimum and of maximum inclination of 0°·365, the difference of the averages of temperatures for 1848–57 and 1857–66 being 0°·339. The latter period of 9¼ years (calculated in both ways) is found to be warmer; and the secular increase of temperature will therefore be from 1°·883 to 2°·028.

Period.

The mean temperature calculated for 1840–53 is 7·428 ...... 13 years.

„   „   „   1854–66 „ 8·035 ...... 13 „

Difference .... 0·607

The secular increase would be 2°·33, a number rather too great; for Mr. Glaisher found a secular increase of 1°·1 C. by means of 30-year periods for London.

On the contrary, the averages of atmospheric pressure during the periods of maximum inclination are greater than those of the periods of minimum inclination :—

Year.	Months.	☊ ☾.	Inclination of the lunar orbit.	Periods of 4 years 8 months.	Average of annual pressure.	Difference.
1848.	3 0	280°	Minimum.	Min. to mean.	329·003‴	
1852.	11·0	90	Mean.	Mean to max.	329·280	−0·277
1857.	6·7	0	Maximum.	Max. to mean.	329·714	
1862.	2·6	270	Mean.	Mean to min.	329·178	−0·536
1866.	9·8	180	Minimum.			

The averages of atmospheric pressure show a diminution of pressure in the minimum periods, and an increase during the maximum periods. During the minimum periods the temperature of the air is higher, the air less dense; in the maximum periods, on the contrary, the air is less warm and more dense.

The periodic increase and decrease of temperature and pressure produced by the variation of obliquity of the lunar orbit may also be ascertained by the averages of midwinter temperatures and midsummer temperatures during the same time; the depression is greater in the winter averages than in the summer averages.

	Winter.	Difference.	Summer.		Period.
1848–52.	2·288°		12·527°		Min. to mean.
1852–57.	1·526	+0·752° R.	12·398	+0·129° R.	Mean to max.
1857–62.	1·880		12·977		Max. to mean.
1862–66.	2·794	+0·914 ,,	13·016	+0·139 ,,	Mean. to min.

The differences of the winter averages are six to seven times as great as those of the summer months (during the seasons of a lunar year of 18½ solar-years).

If the difference of temperature in different seasons of a lunar year is due to the varied obliquity of the lunar orbit, the differences of midsummer and midwinter temperatures must be nearly in a constant ratio, one to another, in the different periods; for the moon's relative positions to the earth will be then symmetrically disposed.

The ratio of those differences is for

$$1848\text{–}52 \text{ and } 1852\text{–}57 : 0·752 : 0·129 = 5·9,$$
$$1857\text{–}62 \text{ and } 1862\text{–}66 : 0·914 : 0·139 = 6·6;$$

that is to say, "the periodic changes produced by the moon during a lunar year are nearly constant."

Another proof of the existence of a periodic change of climate

during a lunar year would be the showing it by means of only one hour of daily observation. It were best to take 9 A.M. for that purpose; for it gives nearly the mean annual temperature.

M. Quetelet has published (in 1867) a series of meteorological observations made in Belgium at 9 A.M., reaching from 1839 to 1863 at Ghent, and from 1847 to 1863 at Liége. The averages of annual temperatures and pressures are :—

			Difference.		Difference.
				millims.	millim.
1838–43.	Max. to mean.	10·32 C.	+0·21 C.	758·84	−0·10
1843–48.	Mean to min.	10·53 „		758·74	
1848–53.	Min. to mean.	10·66 „	+0·16 „	758·84	−0·32
1853–57.	Mean to max.	10·50 „		759·16	

The differences are less perceptible; but they retain their signs, as required by the law.

The averages of annual temperatures and pressures at Liége.

				millims.	millim.
1848–52.	Min. to mean.	10·980 C.	+1·400 C.	754·02	−1·16
1852–57.	Mean to max.	9·580 „		755·18	

The averages of annual temperatures calculated by means of three observations daily made at Elbing (Prussia).

1829–33.	Min. to mean.	7·820	+1·43 R.
1834–38.	Mean to max.	6·394	

It follows that the periodical variations of temperature produced by the moon during half a lunar year is nearly 1°·2 R. (average of the observations of Prague, Liége, and Elbing). Besides, the variations of temperature and pressure are, during half a lunar year, in a constant ratio one to another, as will be perceived by the following data :—

Prague.			Differences of the average	
			Of temperature, Δt.	Of pressure, Δb.
1848–52.	7·881 R.	329·003(P.l.)	+0·959 R.	−0·277(P.l.)
1852–57.	6·922 „	329·280 „		
1857–62.	7·178 „	329·714 „	+1·224 „	−0·536 „
1862–66.	8·402 „	329·178 „		

The ratios of both differences are

$$\frac{1\cdot224}{0\cdot959} = 1\cdot3 \text{ and } \frac{0\cdot536}{0\cdot277} = 1\cdot9\,;$$

therefore the ratio

$$\frac{\Delta t}{\Delta t_1} = \frac{\Delta b}{\Delta b_1} = c$$

is nearly constant.

From the preceding computation of nearly 238,000 observations made at Prague during 1840–66, we may deduce that

(1) When the obliquity of the lunar orbit reaches its highest value the average annual temperature reaches its lowest, and the pressure, on the contrary, its highest value.

(2) The variations of the averages of temperature and pressure are periodical ones, and their period is half a lunar year (of $9\frac{1}{4}$ solar years).

(3) The variations of temperature produced by the lunar influence are more sensible during the winter than during the summer months; for the former are nearly six times the latter.

(4) There must be also another cause, producing a constant increase of temperature, independent of the moon's motion, which may perhaps result from a similar action of the sun on the atmosphere during the period of the change of the obliquity of the ecliptic. The amount of it calculated for a hundred years would be $1°\cdot8$ to $2°$ R.

Prague, April 24, 1868.

LI. *On the Dynamical Theory of Heat.*
By Joseph Gill, *Esq.*

[With a Plate.]

To the Editors of the Philosophical Magazine and Journal.

Gentlemen,

FOUR years ago you were so good as to allow me to state in the Philosophical Magazine some objections to the Dynamical Theory of Heat which I then entertained from the apparent results of numerous experiments on the practical working of steam-engines. At that time I ventured to think that the specific heat of air might possibly vary with its density, though the contrary had been proved by the celebrated experiments of Regnault. Since that time I began again the study of Regnault's " Expériences," particularly respecting the specific heat of gases under different pressures; and while I felt fresh admiration for the wonderful sagacity and fertility of resource displayed in his experiments, and could see no fair reason to doubt his results as to the calorific capacity of air at different densi-

ties, I could not rest satisfied until I had planned a repetition of his principal experiments on this point in a new shape. The only circumstance in his mode of proceeding about which I could have any doubt was the fall of pressure from the varying density of the air in the large reservoir to the constant lower pressure maintained in the calorimetric part of the apparatus; and I imagined it might be more satisfactory, at least as a variation of the experiment, if the heating and cooling worms were traversed by a current of the compressed air from a mass contained in an adjoining reservoir, and caused mechanically to circulate through the apparatus without appreciable change of density or tension.

‑   To effect this I copied as closely as possible the arrangement of Regnault's heating and cooling worms (Pl. VI. fig. 2) *a*, *b*, and added the receiver, *c*, of sheet copper, 7 inches in diameter and 30 inches long, divided into two compartments by the air-tight diaphragm *d*. To this diaphragm is fixed the circulating-pump, *e*—a brass model of a steam-engine cylinder accurately finished, with but slight "lap" and "lead" on the valve, the piston being worked by a handle on the fly-wheel fixed on the outer end of the crank-shaft, *f*, which passes through a stuffing-box on the side of the receiver. The air is taken into the pump through the pipe *g* (the steam inlet-pipe), and discharged into the other compartment of the receiver through the pipe *h* (the exhaust); and it thus circulates in the direction of the arrows, the pump being worked steadily by hand at the given rate. By means of a condensing syringe attached to the tube *k*, the receiver is filled with air of any required pressure above that of the atmosphere, indicated by a pressure-gauge not shown in the figure. The gauge *i* shows the pressure resulting from resistance to the free passage of the air through the worms. At sixty revolutions of the pump per minute the quantity of air at atmospheric pressure passed through the worms corresponds approximately with the mean of Regnault's experiments; then at four atmospheres' pressure fifteen revolutions per minute would send through the worms the same mass of air in equal time; and so on for other densities. Suffice it to say, in a few words, that the results of careful experiments with this apparatus completely confirm Regnault's results, and I have experienced sincere satisfaction from the dissipation of my long pending doubts on this very essential point.

It was well remarked by Hirn that, as the capacity of gases for heat is constant, or nearly so, the facts of the heating and cooling of a gas by compression and expansion are inexplicable and really without a cause, unless we allow a direct relation between the work expended or produced and the heating and cooling of the gas. The same direct relation of cause and effect ought to exist in the case of steam; and as saturated steam can-

not lose heat without a corresponding amount of condensation, the return into water of a portion of the working steam equivalent to the work done seems to be an inevitable conclusion. Hirn's later experiments on the working of large steam-engines, described in his "Exposition Analytique," 1865, seem to prove this relation; and it is now supposed that the anomalous results of former experiments are attributable chiefly to the presence of water in the steam. This point has been fairly proved by the use of superheated steam in Hirn's more recent experiments; and a fresh series of experiments which I have been recently making with a different method, which I believe to be novel, lead to the same conclusion in a manner which does not seem to admit of further doubt on the subject. I shall probably ere long be requesting of you the favour to allow a brief statement of these experiments to appear in the Philosophical Magazine; meanwhile the insertion of the present remarks would much oblige me.

<div style="text-align:center">I remain, Gentlemen,
Your obedient Servant,</div>

Palermo, March 19, 1868.   JOSEPH GILL.

LII. *On the least Electromotive Force by which a Galvanic Luminous Arc can be produced.* *By* E. EDLUND[*].

1. WHEN the conduction between the poles of a powerful voltaic battery is interrupted, and a luminous arc formed at the break, the intensity of the current is known to be considerably less than when the conduction is unbroken, and no light exists. It has hitherto been assumed that the great diminution in the intensity which here ensues arises from a great resistance which the luminous arc offers to the transmission of the current. It has been found that this resistance increases with the length of the arc. In a previous investigation[†] I have proved experimentally that if an ordinary resistance be interposed in the circuit which causes the same diminution as the luminous arc alone, this consists of two parts, one of which is quite independent of the length of the luminous arc, and is unchangeable in magnitude so long as the intensity remains the same; the other part increases proportionally to the length of the luminous arc, provided that, when the length of the arc is increased, so much of the interposed resistance is removed that the intensity of the current is not thereby diminished. If the

first part of the resistance in question be called a, and the other part, corresponding to a luminous arc of unit length, is b, the resistance of a luminous arc whose length amounts to n units is $a + nb$. It follows from the experimental part of the research in question that a is inversely as the intensity. It is therefore easy to calculate the length of a for a certain intensity, provided its value is known for another. The resistance b also increases in magnitude if the intensity decreases, although the law for this increase could not be deduced from the experiments, because b for the unit of length assumed was so small, in comparison with a, that no accurate measurements in this respect could be made.

If, then, the length of the luminous arc be increased while at the same time the intensity is not kept constant by shunting out some resistance, the intensity is diminished for two reasons: first, the quantity $a + nb$ is increased by n being increased, even if a and b were unchangeable ; and, secondly, a and b increase in magnitude if the intensity is diminished.

The circumstance alone that a is independent of the length of the luminous arc throws suspicion on the nature of its resistance. In this manner a voltaic resistance would have been found which, independently of other resistances, would be independent of the length of the conduction. In the research in question I have shown how, by the aid of the mechanical theory of heat, it may be demonstrated that the diminution in the intensity of the current represented by a is not caused by a resistance, but is due to an electromotive force which sends a current in an opposite direction to the principal current. If, now, the magnitude of the electromotive force be calculated which would produce as great a diminution in the intensity as the resistance a (which is inversely as the intensity), we find that this electromotive force (D) is independent of the intensity. But this conclusion, that D is independent of the intensity, or, in other words, that a is inversely proportional to it, depends on experiments which were made with powerful currents; practical difficulties presented themselves in the attempt to keep the luminous arc constant for some time when the intensity was small; hence it might be very possible that D was only constant at a certain limit of intensity, but varied with the intensity below this limit. This seemed to me not at all improbable, especially as some similar phenomena exhibit a similar deportment; the force of voltaic polarization, for instance, increases with the intensity up to a certain limit, and is then constant. Hence I determined to make new observations.

2. Since the method which I used in my former research to determine D is inapplicable (for the reasons adduced) when the intensity is small, another method had to be employed. If D is ac-

tually independent of the current, it is impossible to obtain a luminous arc when the electromotive force (E) of the battery is so much diminished that E is equal to D ; the sum of the electromotive forces of the entire circuit is then zero, and hence the current must cease. But even before E, in being diminished, attains these limits, the impossibility of forming a luminous arc must occur; for a certain intensity is necessary for its formation, the magnitude of which depends partially on other circumstances—as, for instance, the shape of the poles, the length of the arc, &c. If, now, it should appear that a luminous arc may be produced when E is as small as, or smaller than that value of D which is obtained in experiments with strong currents, this must be regarded as a certain proof that in feebler currents D is independent of their magnitude.

3. It is the characteristic of the voltaic arc that material particles are carried by the current from one pole to the other, and that conduction is effected mainly by this transference. It is often difficult to determine with certainty by the external appearance whether there is a true luminous arc or not. When there is an actual though imperfect contact between the poles, the ignition and the combustion which generally follows the former may be so great when the experiment is made in the open air, that the phenomenon has the same appearance as if there were a true voltaic arc. Hence it is easy to make a mistake in this respect, if the external appearance only be taken into consideration. In order to avoid such errors, a key with a shunt was interposed in one of the wires leading from the battery to the place where the luminous arc was to be formed. In some experiments there was a tangent-, and in the others a sine-compass in the shunt. In one position of the key the principal circuit was closed and the secondary one open ; in the other it was just the reverse ; and in the latter case the current could traverse the secondary circuit, avoiding the break in the principal circuit. When the light between the poles was really so bright as to resemble an actual arc, the key was brought from the first into the second position. During this the conduction was interrupted long enough for the luminous arc to be extinguished. If the poles were in contact, the magnetic needle made a deflection after the reversal, and the poles again began to be ignited; but if the luminous phenomenon was produced by a true voltaic arc, the magnetic needle remained at rest. This mode of investigating whether there was a true voltaic arc or not, was of course only needed when the intensity of the current was small, and the voltaic arc so short that it could not be directly seen whether the points were apart or not.

The experiments were made as follows*:—After the electromotive force of the battery and the resistance had been determined when the poles were screwed against each other, the electromotive force D in the luminous arc was measured by the rules given in my former investigation. For this purpose the points were fitted in a pole-holder which was placed in a Foucault's lantern, and the length of the luminous arc determined by measuring the image projected on the screen. The pole-holder was then removed from the lantern and firmly screwed against the table, upon which the electromotive force of the battery was successively diminished by the removal of a greater or smaller number of elements. At each diminution of the electromotive force, it was examined whether a luminous arc could be formed or not, until the limit was reached. The trough which I mentioned in my former paper was used as a rheostat, and was filled with sulphate of copper. In all the following experiments the line joining the poles was vertical, in my first investigation it was horizontal.

First Series.

Experiment 1.—The battery consisted of sixty-six Bunsen's elements. Hard charcoal was used for the pole-points. When the points were in contact and there was an inch of the rheostat in the circuit, the tangent-compass indicated 56° 26′, and when there were 10 inches, 38° 30′. From this it may be calculated that the entire resistance M besides the rheostat was $= 9\cdot067$, and the electromotive force of the battery E was $15\cdot171$, that force being taken as unity which produces a deflection of 45° in the tangent-compass when the resistance was 1.

When a luminous arc having a length of three divisions of the scale was formed and an inch of the rheostat was interposed, the deflection was equal to 37° 30′; and when 11 inches were interposed it gave the same deflection. With the same intensity there was obtained:—

The resistance in the arc of two divisions $= 8\cdot9$

,,　　　　,,　　one　,,　$= 7\cdot7$

From this we obtain $a = 6\cdot6$, and $b = 1\cdot15$. The electromotive force of the battery and the resistance in the conduction was then measured afresh without the rheostat, and there was obtained $M = 8\cdot527$, and $E = 15\cdot73$. During these experiments the mean, therefore, was $M = 8\cdot797$, and $E = 15\cdot451$.

We thus get $D = \dfrac{6\cdot6}{19\cdot797} = 0\cdot3334E = 5\cdot15$.

Experiment 2.—Thirty elements. A distinct luminous arc

was obtained with this. In these experiments M=3·41, and E=7·20.

Experiment 3.—Twenty-five elements. This occasionally gave a distinct luminous arc. M=2·96, and E=6·00.

Experiment 4.—Twenty elements. With these elements a uminous arc could not be obtained, although the carbon-points became strongly incandescent in the interval, which resembled a true light. M=2·58, and E=4·60.

Second Series.

The pole-points were of brass containing about 37 per cent. of zinc.

Experiment 5.—The battery consisted of sixty-six elements. M=9·25, and E=17·26.

When 1 inch of the rheostat was interposed and the length of the arc was three divisions, the tangent-compass was at 52°. With this intensity there was found :—

The length of the arc 3 divisions, its resistance = 2·8
,,　　　　,,　　2　　,,　　　　　,,　　　= 2·6

From this we obtain a=2·2, and b=0·2.

Thereupon the resistance and the electromotive force were again determined; they were found to be M=10·71, and E=18·57. The mean in these experiments was M=9·98, and E=17·92. From this we calculate

$$D = \frac{2·2}{13·78} \times E = 0·1597E = 2·86.$$

Experiment 6.—Twenty elements. With these we get a distinct luminous arc. M=1·56, and E=3·65.

Experiment 7.—Fifteen elements. A distinct arc could be obtained with this electromotive force. In these experiments M=0·84, and E=2·65.

Experiment 8.—In this experiment only ten elements were used, and no arc could be produced by them. The resistance and the electromotive force were measured, and were found to be M=0·32, and E=1·60.

Third Series.

For the pole-points in this series, carbon was used which had been sawn out of a piece of broken battery carbon. It appeared to be softer than the carbon used in the first series.

Experiment 9.—The battery consisted of sixty-six elements. M was found =7·56, and E=13·48.

When 2 inches of the rheostat were brought into circuit and a luminous arc of four divisions formed, the tangent-compass

gave a deflection of 34°. For the same intensity we have :—

The length of the arc $= 4$ divisions, its resistance $= 11\cdot0$
,,   ,, $= 4$,,   ,, $= 9\cdot5$

From this we have $a = 8\cdot0$, and $b = 0\cdot75$.

The electromotive force and the resistance were measured anew; the first was $E = 15\cdot34$, and the latter $M = 8\cdot51$. The mean in this experiment was $M = 8\cdot04$, and $E = 14\cdot41$. From this we may calculate

$$D = \frac{8}{21\cdot04} \times E = 0\cdot38E = 5\cdot48.$$

Experiment 10.—Twenty-five elements of the battery were used, which gave a distinct luminous arc. M was found $= 2\cdot55$, and $E = 5\cdot49$.

Experiment 11.—The battery consisted of twenty elements, but no luminous arc could be produced by them. M was found on measurement $= 1\cdot99$, and $E = 4\cdot23$.

Fourth Series.

Copper wires were used for pole-points.

Experiment 12.—The battery consisted of sixty elements. The electromotive force was $16\cdot35$, and the resistance $M = 8\cdot45$.

When 2 inches of the rheostat were introduced into the circuit and the length of the luminous arc was four divisions, the deflection on the tangent-compass was $46° 30'$. With the same intensity there was obtained :—

Length of the arc 4 divisions, its resistance $= 4\cdot9$
,,   ,,   2 ,,   ,, $= 4\cdot6$

From this we have $a = 4\cdot3$, and $b = 0\cdot15$.

The electromotive force and the resistance were next measured, and gave $M = 9\cdot84$, and $E = 17\cdot83$. The mean of this experiment was therefore $M = 9\cdot14$, and $E = 17\cdot09$.

From this we find that

$$D = \frac{4\cdot3}{16\cdot04} \times E = 0\cdot268E = 4\cdot58.$$

Experiment 13.—The battery consisted of twenty elements, with which a distinct luminous arc was obtained. M was here $= 1\cdot56$, and $E = 4\cdot65$.

Experiment 14.—With the fifteen elements of which the battery consisted, no luminous arc could be produced. M was found, on measurement, to be $1\cdot30$, and $E = 2\cdot98$.

Experiment 15.—This was made with twenty elements, a few days after the latter, and a distinct luminous arc obtained. On measuring, E was found $= 3\cdot51$, and $M = 1\cdot23$.

Experiment 16.—This was made immediately after the last; the battery consisted of fifteen elements, with which, however, no luminous arc could be produced. M was $=0\cdot86$, and $E=2\cdot55$.

Fifth Series.

Silver, said to contain 10 per cent. of copper, was used for the pole-points.

Experiment 17.—The same sixty elements were used for the battery as formerly. On measuring, M was found $=8\cdot02$, and $E=12\cdot75$.

When two inches of the rheostat were introduced into the circuit, and the length of the luminous arc was three divisions, the tangent-compass was at 43°. With the same intensity we had :—

The length of the arc 3 divisions, its resistance $=4\cdot4$
” ” 1 ” ” $=3\cdot3$

From this we calculate $a=2\cdot75$, and $b=0\cdot55$.

The resistance and the electromotive force were next determined, and there was obtained $M=8\cdot67$, and $E=14\cdot03$. Hence in the mean we had the values $M=8\cdot34$, and $E=13\cdot39$.

From this we find $D=\dfrac{2\cdot75}{14\cdot74}\times E=0\cdot1865E=2\cdot5$.

Experiment 18.—Fifteen elements were used for the battery, which gave a light when the pole-points were suitably shaped. In this case $M=0\cdot92$, and $E=2\cdot64$.

Experiment 19.—In this experiment twelve elements were used. A luminous arc was only occasionally produced, and especially when the poles had the shape which had been imparted to them by a powerful current. The measurements gave $M=0\cdot72$, and $E=1\cdot89$.

4. It is seen, from what has been said, that M and E varied to no inconsiderable extent even in one and the same experiment. Hence it was not possible to determine with the desired accuracy the value of D. Meanwhile these values are not to be looked upon as too untrustworthy,—partly because the resistance and the electromotive force of the battery were determined both *before* and *after* the experiments which were made for the determination of D, and therefore their mean may be regarded as valid for the time in which the latter operations were made; partly also because M and E, with the exception of Series 1, both increase simultaneously, owing to which their variations, in the determination of D, partially compensate one another. In seeking the smallest value of E with which a luminous arc could be produced, a great number of observations was always made. Although several successive experiments failed in producing a luminous arc, it occasionally happened that it could be done by repeatedly

trying. The luminous phenomenon was frequently so brilliant as to make it appear as if there was an actual luminous arc ; but when the circuit was opened and the conduction examined in the usual manner, it was found to be a mere ignition with contact between the poles.

If D were quite constant and independent of the intensity, the least electromotive force by which a luminous arc could have been produced must have been greater than D, as determined by the stronger currents. This is obvious ; and it follows, more-over, that if with a given value of E a luminous arc can be produced, this is no longer possible if the resistance is adequately increased. Hence a certain intensity is necessary to produce a luminous arc. Comparing the values of D as determined by stronger currents with the limiting values of E by which a lumi-nous arc can just be produced, it is observed that with the hard carbon-points in Series 1 the electromotive force E of the battery is greater than D, but in all the other series E is either just as great as, or is smaller than D. If the values of D in all the five series are added, and in the same way the limiting values of E, the sum in the first case is 20·57, and in the other 19·57. Hence, as the result of this investigation, we may establish the principle *that* D, *which is constant with powerful currents, diminishes with smaller ones.*

LIII. *On* Grove's *Battery.*
By G. W. Wigner, *F.R.A.S.*[*]

IN the course of a large number of experiments with Grove's batteries in which great electromotive force was required, several modifications of the usual arrangement have suggested themselves to me, which have had the effect of greatly increasing the power of the battery, increasing the constancy of the current, and diminishing the labour of charging the cells.

The first object sought was to diminish the internal resistance of the battery ; and this was attained in four ways.

(1) The upper face of each zinc plate (to which the pla-tinum plate is screwed) was carefully filed off to a perfectly smooth and flat surface, and the screws were tightened as much as possible. A large contact-surface was thus secured instead of the few points at which it is usually obtained. The oxidation between the two plates was also greatly diminished by this. The contacts of course were carefully cleaned every time the battery was used.

(2) The thickness of the platinum plates was increased, as it

was found that when of the ordinary thickness they opposed a serious resistance to the current.

(3) The zinc and platinum were brought much nearer together, thus diminishing the length of liquid through which the current had to pass in each cell. In many cases the zinc plates were put into absolute contact with the porous cell without any apparent disadvantage.

(4) A *white* porous cell of a very close and uniform texture was at last selected, as embracing both the necessary conditions of good conducting-power and pores sufficiently small to prevent the free mixture of the acids.

The second object sought was to prevent local action; and this was accomplished by putting a small quantity of mercury at the bottom of each cell, in contact with the zinc, which was by this means always thoroughly amalgamated. Ultimately the zincs were made in two pieces—one flat piece $4\frac{1}{2} \times 3$ for one side of the cell, the other a bent piece to carry the platinum; and the connexion between the two pieces was formed by the mercury at the bottom of the cell. This alteration was found to be a great convenience, as any zinc could be lifted out without disturbing the adjoining cells. It also proved economical, the first cost of each zinc being less and the durability greater; for the old shape always broke at the lower bend long before they were worn out.

Anothe source of loss still remained, in the short circuits which were formed from one cell to another, and from the terminals to the ground, by moisture and condensed acid, and which, when working with 120 cells, were so strong as to render it painful to touch the terminal screws of the battery while standing on a stone floor.

To obviate this, two glass rods about half an inch in diameter were fixed lengthwise in the bottom of each tray, and on these rods the cells stood; thus any moisture which might *condense* settled out of contact with the cells. The trays and small pieces of wood which were inserted between each cell were of oak, baked for twelve hours, and varnished with three coats of shell-lac varnish; and when in use each tray (of ten cells) was insulated by another series of glass rods; so that the loss by local circuits was reduced to a minimum.

I have also found considerable advantage from working the batteries in front of a large fire: the fumes of the acid are all carried up the chimney, and condensation very greatly diminished.

I next endeavoured to increase the constancy of the battery.

The first step, of course, was to increase the dimensions of the outer cells, to prevent the sulphuric acid from becoming so rapidly saturated with zinc. I then tried the effect of stronger nitric acid, even as high as 1·540 spec. grav., but eventually decided

in favour of nitrosulphuric acid; and the results I have obtained are very satisfactory, amounting in one case to a loss of only 18 per cent. in the light, ten hours after setting up the batteries, more than six hours of which the batteries were in circuit. If only four or five hours' work is required from the battery, 2 lbs. nitric acid (1·360 spec. grav.) to 5 lbs. sulphuric acid (1·845 spec. grav.) will be a very good proportion; but if more work is required, the proportion of nitric acid may be increased to $3\frac{1}{2}$ lbs. I once worked sixty cells very satisfactorily for four hours with only 1 lb. nitric to 5 lbs. sulphuric.

I do not find that any excessive action on the zinc takes place owing to this change; and its economy as regards the acid is self-evident.

The diluted sulphuric acid which I use is generally 1 to 6 by bulk.

Now a few words as to the mode of filling the cells.

The old plan of jug and funnel is slow and unsatisfactory; and I have adopted with great success the siphon principle, as follows. I mix the acids in two large stone bottles fitted with corks having two holes in each. Through one of these holes a glass tube passes to the bottom of the bottle, bent over outside for some two or three inches. Attached to this is a piece of *india-rubber tube* about 6 feet long, with a jet not more than 3 inches in length at its end. This jet is formed of a piece of glass tubing, slightly flattened in the lamp, for convenience in inserting it into the cells. To regulate and stop the flow of the acid, I use one of Mohr's *spring* pinchcocks, which clamps the india-rubber tube. The other hole in each cork is for a blowing-tube, passing a very short distance into the bottle, to charge the siphons with. These being once charged, it is very easy to pass the jet from cell to cell (stopping the acid meanwhile by the pinchcock) without spilling a single drop; and so quickly can this be done, that I have repeatedly charged sixty cells with both acids (without assistance) in from 20 to 25 minutes. The bottles, of course, should stand some four feet above the level of the battery. The india-rubber tube should be rinsed out immediately after use, with water containing a little alkali; it will then last for a very long time.

As to the results which I have obtained by these various alterations, it will perhaps be sufficient to give a few measures of the power of the light between charcoal-points reduced to standard sperm candles. They are as follows:—

Sixty cells as usually constructed and put $\left.\right\}$ 1860 candles. together gave a light of . . . . . $\left.\right\}$
      Size of platinum $5 \times 2\frac{1}{4}$.

Sixty cells as above, but with zincs carefully filed . . . . } 2930 candles.

Do. insulated with glass rods, nitrosulphuric acid, mercury in cells, &c. Average of nine measures . . . . } 5360 „

By way of comparison I have taken the following three measures of the light from batteries of the same size in use in London :—

No. 1.	. .	50 cells.	1560 candles.
„ 2.	. .	50 „	926 „
„ 3.	. .	60 „	976 „

These vary greatly, but form, I should think, a very fair average.

LIV. *Chemical Notices from Foreign Journals.*
By E. Atkinson, *Ph.D., F.C.S.*

FRIEDEL and Ladenburg* have described an oxychloride of silicon. A porcelain tube, either empty or filled with fragments of felspar, was heated to nearly the fusing-point of the latter, and chloride of silicon passed over it. On repeating this operation several times with the liquid which had passed over, and subsequently rectifying the product thus obtained, it was separated into chloride of silicon and a liquid boiling mainly between 136° and 139°. It resembles chloride of silicon in its deportment with water, by which it is decomposed into silicic and hydrochloric acids. The determination of the chlorine gave numbers for the body corresponding to the formula $Si^2 \Theta Cl^6$†; this formula is confirmed by the action of the body on absolute alcohol, with which it forms a body called *hexethylic disilicate,* which had already been obtained by Friedel and Crafts by the action of aqueous alcohol on orthosilicate of ethyle. The constitution of the bodies may be thus written :—

$$\Theta \left\{ \begin{array}{l} Si\,(C^2H^5\Theta)^3 \\ Si\,(C^2H^5\Theta)^3, \end{array} \right. \qquad \Theta \left\{ \begin{array}{l} Si\,Cl^3 \\ Si\,Cl^3. \end{array} \right.$$
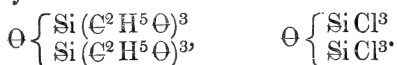
Another argument for the formula of the oxychloride is its action on zincethyle, with which it yields the body oxide of silicium triethyle, $\Theta \left\{ \begin{array}{l} Si\,(C^2H^5)^3 \\ Si\,(C^2H^5)^3. \end{array} \right.$

It seems most probable that the oxygen in the compound is

* *Comptes Rendus,* March 16, 1868.
† Si = 28.

derived from the felspar; for this is seen to be attacked, and there are fused drops of alkaline chloride. But it is difficult to determine the precise nature of the reaction. It is most probable that chloride of silicon gives to the alkaline silicate part of its chlorine in exchange for an equivalent quantity of oxygen.

Comparing the formulæ for the new body and for perchlorinated methylic oxide,

$$O \begin{cases} Si\,Cl^3 \\ Si\,Cl^3, \end{cases} \qquad O \begin{cases} C\,Cl^3 \\ C\,Cl^3, \end{cases}$$

their analogy is at once seen; and in accordance with it the authors suggest as a name for the body either *perchlorinated silicimethylic ether,* or *oxide of trichlorosilicium.*

Schützenberger[*] has described the following method for the preparation of phosgene gas, which does not require the presence of sunlight. When a mixture of carbonic oxide and vapour of tetrachloride of carbon is passed over pumice heated to about 350°, the following action takes place:—

$$2\,C\,Cl^4 + CO = 2\,(CO\,Cl^2) + C^2\,Cl^4.$$
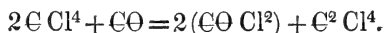
The quantity produced under these conditions is considerable, and the reaction may be used in practice.

The carbonic oxide may with equal success be replaced by carbonic acid, which gives

$$C\,Cl^4 + CO^2 = 2\,CO\,Cl^2.$$
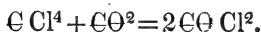
In trying the above reaction, using spongy platinum instead of pumice, the formation of considerable quantities of oxychloride was observed; but it was also noticed that the platinum acted otherwise than by its presence. A platinum compound is formed which may be collected in the cool parts of the tube as a bright-yellow flocculent powder. As the new compound is destroyed at a temperature a little higher than that at which it is formed, it is important that the current of carbonic oxide be rapid, so that the body may be carried away as rapidly as it is formed. The new body melts at about 150° to a deep-yellow transparent liquid, which solidifies on cooling as a yellow crystalline mass. At about 350° to 400° it boils and distils, but is mainly decomposed into metallic platinum and oxychlorocarbonic acid. Water decomposes it at once with formation of carbonic acid and finely divided platinum, while the liquor gives the reactions of hydrochloric acid. The analyses lead to the formula $(CO)^3\,Pt^2\,Cl^4$; but further experiments are necessary for settling this point.

[*] *Comptes Rendus,* April 13, 1868.

Than* has described an oxysulphide of carbon having the formula COS, and which therefore may be regarded as carbonic acid in which an atom of oxygen is replaced by sulphur. It may be prepared in no inconsiderable quantities by passing carbonic oxide with excess of sulphur vapour through a red-hot porcelain tube; it is, however, mixed with carbonic oxide, from which it could not be separated. The method of preparing the gas in a pure state depends on the following theoretical considerations. Hydrated cyanic acid may be most simply regarded as the imide of carbonic acid, $(CO)'' HN$; and in its decomposition with water carbonic oxide is replaced by two atoms of hydrogen, by which ammonia and carbonic acid are formed, in accordance with the equation

$$(CO)'' HN + H^2O = H^3N + CO^2.$$
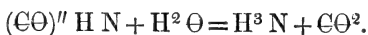
If this be the case, hydrosulphocyanic acid should yield by the action of dilute acids ammonia and oxysulphide of carbon,

$$(CS)'' HN + H^2O = H^3N + COS.$$
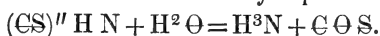
Experiment has confirmed this supposition most completely. When powdered sulphocyanide of potassium is added to a cold mixture of sulphuric acid and water, a disengagement of the gas in question ensues, which may be easily controlled by increase or diminution of temperature so as to have a regular current. The gas is passed through a tube containing cotton rubbed with moist oxide of mercury to retain acids (hydrocyanic and probably a trace of formic), through a tube containing very small pieces of unvulcanized india-rubber to retain bisulphide of carbon (which can be recommended as a most effectual means for the purpose), and, lastly, through a third tube containing chloride of calcium. The purified and dried gas is collected over mercury. If both be quite dry, the gas may be preserved for some days without any change; but if there be any moisture, the surface of the mercury becomes coated with sulphide in the course of a few hours.

The gas thus purified has an odour resembling carbonic acid, which at the same time suggests the odour of resin and sulphuretted hydrogen, but is not unpleasant. Water absorbs about an equal volume of the gas, and acquires its odour; but immediately afterwards it changes into the peculiar sharp stinging taste, suggestive of both sulphuretted hydrogen and sulphurous acid.

The density of the gas (2·1046) is twice that of air, and it can therefore be poured from one vessel into another. The substance has a feebler acid reaction than carbonic acid.

It is very inflammable, being immediately inflamed even by a scarcely glimmering spill. It burns with a beautiful blue and

* Liebig's *Annalen*, (Suppl.) vol. v. p. 236.

not strongly luminous flame, forming carbonic and sulphuric acids. If a lighted taper be dipped into the gas, the gas is inflamed but the taper extinguished, as with a jar of hydrogen the mouth of which is held downward. With $1\frac{1}{2}$ volume of oxygen it forms an explosive mixture.

Potassic hydrate and other alkaline hydrates absorb the gas as completely as carbonic acid, though somewhat more slowly. The solution is inodorous, but disengages sulphuretted hydrogen and carbonic acid when treated with acids. It is probably decomposed as follows :—

$$COS + 4KHO = K^2CO^3 + K^2S + 2H^2O.$$
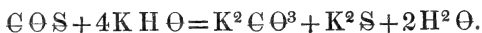
The solution gives with ammoniacal solution of silver a copious black precipitate, and the filtered solution indicated no trace either of chlorine or cyanogen.

Neither chlorine nor fuming nitric acid exert any action on the gas at ordinary temperatures. When sodium is heated in the gas it burns with a dazzling light, forming a black easily fusible mass, which consists of carbon, sulphide of sodium, and carbonate of sodium. By heating, the gas is decomposed into sulphur and carbonic oxide without any change of volume.

The analysis of the gas left no doubt as to its composition being COS, according to which its molecular weight is 60. Its theoretical density according to this is 2·08, while the density observed was 2·109.

Than thinks that this gas is pretty widely distributed in nature.

The following observations on the preparation of metallic cerium have been made by Wöhler*. A solution of ordinary brown oxide of cerium in hydrochloric acid was evaporated to dryness with an equal quantity of chloride of potassium and of sal-ammoniac; the mixture was then heated in a crucible until all the sal-ammoniac was volatilized; and the mass, having been allowed to cool, was broken in small pieces; and having been mixed with metallic sodium, the mixture was projected into a red-hot crucible. On raising the heat a crackling noise was heard, which indicated a reduction; the action of the fire was continued until all the sodium had been volatilized and the mixture was perfectly fluid. On cooling, the dark-grey mass was found to contain numerous small metallic globules.

These appeared to consist of metallic cerium. Its colour is between that of iron and that of lead, and when polished it displays a tolerably strong lustre. It is malleable, and can be cut almost as easily as lead. Its specific gravity is about 5·5. It gradually loses its lustre on exposure to the air, acquiring a blue

* Liebig's *Annalen*, November 1867.

coating. In boiling water it disengages a small amount of hydrogen. Gently heated in the air it burns, with formation of brown oxide; but if suddenly heated more strongly, it burns with explosive violence, and scatters about the most brilliant stars. In this respect it differs from everything, with the exception of uranium.

Bettendorff[*] has described two allotropic modifications of arsenic. When pure arsenic was volatilized in a rapid current of hydrogen, metallic hexagonal arsenic was deposited in the immediate neighbourhood of the heated part, and a little further on there was some black amorphous arsenic, while the whole front part of the tube was filled with a bright yellow fume, which as it deposited became darker and finally grey. It was found on analysis to be pure metallic arsenic; it was quite amorphous, and was found under the microscope to consist of small globules arranged together in a chaplet-form. Its specific gravity was found to be 4·71; and when heated from 358° to 360° it changes into crystalline metallic arsenic of the specific gravity 5·72, with such disengagement of heat that part of the arsenic volatilizes.

The black amorphous arsenic with a vitreous lustre is obtained when arsenic vapour is cooled to from 210° to 220°. It is best prepared by bending one end of a combustion-tube in a U-shape, and immersing this part in an oil-bath heated to 220° while the arsenic, which is placed near the upper end of the tube, is volatilized in the current of hydrogen. After the experiment the interior of the U-tube is lined with a splendid mirror, which by gently tapping is obtained in a number of thin brittle scales. Its specific gravity is 4·71; and on heating to 360° it passes into crystalline arsenic, with considerable development of heat. It resists chemical attack much more energetically than crystallized arsenic.

Gondolo[†] has described an important modification in Boussingault's method of preparing oxygen. Tubes either of wrought or cast iron are covered on the inside with a lute of magnesia, and externally with asbestos, in order to diminish the porosity and the waste in the fire. These tubes are fastened in a brick furnace provided with arrangements for regulating the draught so that the tubes can be heated either to bright or to dull redness. The tubes contain baryta, with which is mixed lime, and a small quantity of manganate of potash, which prevents fritting. Air is then passed through the tubes at a low heat, at which the

oxygen is absorbed with formation of binoxide of barium; on heating this to a higher temperature pure oxygen is given off.

The author has effected in this manner, without cessation, as many as 122 alternations of oxidation and deoxidation, and thus separated by an easy and practical process the oxygen from the nitrogen of the air.

The following method of Bothe for the same purpose is a modification of one devised by Tessié du Motay and Maréchal*. It is based on the following reactions :—Peroxide of manganese mixed with soda, and submitted to a high temperature in contact with air, is changed into manganate,

$$MnO^2 + Na^2 O + O = Mn Na^2 O^4.$$
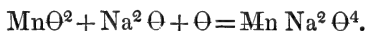
This manganate gives up part of its oxygen at 450° under the influence of aqueous vapour,

$$Mn Na^2 O^4 + H^2 O = MnO^2 + Na^2 O + H^2 O + O.$$

The apparatus used by Bothe in his experiments is a cast-iron cylinder a metre in length by a third of a metre in diameter. This is divided into two parts by a plate perforated with holes. In the front part of the crucible is a spiral iron tube in which the steam is superheated; after traversing this tube the steam passes through the apertures to the middle of the retort and acts on the manganese; then, mixed with oxygen, it traverses a worm where the steam is condensed, while the oxygen passes into a gas-holder whence it can be used. When the reduction is complete, a current of air is passed over the mixture of peroxide of manganese, which at a red heat becomes changed into manganate, which can again furnish oxygen, and so on.

M. Fizeau†, in continuing his researches on the expansion of bodies by heat, has observed that iodide of silver forms an important exception to the ordinary law of expansion. The substances he examined were the chlorides of potassium, sodium, ammonium, and silver, bromide of potassium, iodides of potassium, mercury, lead, and cadmium. All of these experience a considerable increase in volume by heat, an increase which is even higher than that of the most expansible metals, such as zinc and lead. Yet iodide of silver, which both in chemical composition and general relations belongs to this group, constitutes a very important exception; it contracts by heat and expands by cold : the phenomenon is perfectly regular and continuous be-

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* *Bulletin de Chimie*, December 1867.
† *Comptes Rendus*, vol. lxiv. p. 314, *Bulletin de la Société Chimique*, September 1867.

tween 10° and 70° C. As iodide of silver melts only at a rather high temperature (400° C.), the effects could not be attributed to the irregularities which might be produced in the neighbourhood of the temperature corresponding to the change in condition of the substance.

The expansion of iodide of silver should thus be expressed by a negative coefficient—at any rate, within the above limits. Moreover, in proportion as the temperature rises, the value of the coefficient considerably increases, so that the contradiction becomes more and more marked.

Haagen has determined the refractive indices and specific gravities of some liquid haloid compounds[*]. Two of Meyerstein's spectrometers were used for ascertaining the refractive indices. By means of the larger one, which had a vernier reading to ten seconds, the index could be determined with certainty to the fourth place of decimals, and with a possible error of four units in the fifth place. By the smaller instrument, which was used for investigating fuming chlorides, the angle could be read off to a minute; the indices determined with its aid were accurate to the third place; the fourth varied by three or four units. The method used was that of the least deviation. A Geissler's hydrogen-tube was used as a source of light, and the refractive indices determined in reference to the three principal lines of the hydrogen-spectrum, of which the red one (α) notoriously coincides with Fraunhofer's line C, the green (β) with F, while the violet (γ) lies between G and H.

The refractive indices were all made at the temperature 20°. The liquid to be determined was contained in a hollow prism, and its temperature indicated by a delicate thermometer with a small bulb. The prism was heated in an air-bath a few degrees above 20°, then placed on the spectrometer, and the least deviation of a ray determined when the temperature had exactly sunk to 20°. Repeated observations after fresh heating never varied from each other more than 10, or at most 20 seconds, which makes a difference in the refractive index of four to eight units in the fifth decimal.

The constants of Cauchy's formula, $\mu = A + \dfrac{B}{\lambda^2}$, were calculated from the refractive indices for the red and the violet ray. Putting

$$\mu_\alpha = A + \frac{B}{\lambda_\alpha^2}, \text{ and } \mu_\gamma = A + \frac{B}{\lambda_\gamma^2},$$

[*] *Zeitschrift für Chemie,* January 25, 1868.

we obtain

$$B= \frac{\mu_\gamma-\mu_\alpha}{\frac{1}{\lambda_\gamma^2} - \frac{1}{\lambda_\alpha^2}}, \quad A=\mu_\gamma-\frac{B}{\lambda_\gamma^2},$$

and, introducing the values for the wave-lengths expressed in hundred-thousandths of a centimetre,

$$\lambda_\alpha=6\cdot564, \text{ and } \lambda_\gamma=4\cdot339 \text{ (Plücker)},$$

$$B= \frac{\mu_\gamma-\mu_\alpha}{0\cdot029906}, \quad A=\mu_\gamma-\frac{B}{18\cdot227}.$$

The specific gravities of the liquids were also accurately determined for the temperature 20°, as compared with the specific gravity of water for the same temperature. The boiling-points of the substances were determined by means of accurate thermometers, and were corrected for that part of the mercurial thread which projects out of the retort.

The author then gives the particulars of a number of his experiments, from which the refractive equivalents of a number of elements may be calculated from the refractive equivalents of their compounds. For calculating the refractive equivalent, the author used the formula $P\frac{\mu-1}{d}$, in which P is the atomic weight and $\frac{\mu-1}{d}$ is the specific refractive equivalent. If R is the refractive equivalent of a compound, $r, r', \ldots$ those of its elements, and $m, m', \ldots$ the number of atoms as expressed by the chemical formula, the relation holds good,

$$R=mr+m'r'+m''r''+ \ldots,$$

from which the refractive equivalent of any element may be calculated, knowing those of the others as well as R ; for

$$r=\frac{R-m'r'+m''r''}{m}.$$

Landolt has calculated the refractive equivalents of the elements carbon, hydrogen, and oxygen from the refractive equivalents of the liquid compounds, and assuming the refractive index μ_α, and the atomic weights $H=1, O=16, C=12$, has obtained the following values :—

$$H_\alpha=1\cdot30; \quad O_\alpha=3\cdot00; \quad C_\alpha=1\cdot50.$$

By the aid of these numbers the refractive equivalents of the haloids may be calculated from the liquid compounds they form

with C and H. The value thus obtained for chlorine renders it possible to establish the refractive index of those elements which form liquid chlorides.

The author has ascertained the refractive equivalents not merely in reference to μ_α, but also by the aid of Cauchy's formula of dispersion. For this purpose the values $P\dfrac{A-1}{D}$ of H, Θ, and C had first to be calculated from Landolt's observations, which gave

$$H_A = 1{\cdot}29 \; ; \;\; \Theta_A = 2{\cdot}90 \; ; \;\; C_A = 4{\cdot}86.$$

The following Table gives the specific refractive capacity $\dfrac{\mu_\alpha - 1}{d}$ and $\dfrac{A-1}{d}$, as well as the resulting refractive equivalent obtained by multiplication with the molecular weight P :—

		P.	$\dfrac{\mu_\alpha-1}{d}$.	$\dfrac{A-1}{d}$.	$P\dfrac{\mu_\alpha-1}{d}$.	$P\dfrac{A-1}{d}$.
Tetrachloride of carbon...	C Cl⁴	154	0·2871	0·2797	44·21	43·07
Chloroform	C H Cl³	119·5	0·2974	0·2895	35·54	34·60
Chloride of ethylene......	C² H⁴ Cl²	99	0·3519	0·3436	34·84	34·02
Bromide of ethyle	C² H⁵ Br	109	0·2886	0·2805	31·46	30·57
Bromide of amyle.........	C⁵ H¹¹ Br	151	0·3641	0·3547	54·98	53·56
Bromide of ethylene	C² H⁴ Br²	188	0·2446	0·2364	45·98	44·44
Iodide of methyle	C H³ I	142	0·2316	6·2213	32·89	31·42
Iodide of ethyle............	C² H⁵ I	156	0·2626	0·2517	40·96	39·27
Iodide of amyle............	C⁵ H¹¹ I	198	0·3306	0·3199	65·46	63·34
Bisulphide of carbon......	C S²	76	0·4876	0·4517	37·06	34·33
Chloride of sulphur	S² Cl²	135	0·3825	......	51·64	
Terchloride of phosphorus	P Cl³	137·5	0·3222	0·3141	44·30	43·19
Terchloride of arsenic ...	As Cl³	181·5	0·2732	0·2613	49·59	47·43
Terchloride of antimony .	Sb Cl³	299·5	0·2491	......	74·61	
Tetrachloride of tin......	Sn Cl⁴	260	0·2271	0·2183	59·05	56·76
Tetrachloride of silicon...	Si Cl⁴	170	0·2768	0·2702	47·06	45·93
Chloride of sodium	Na Cl	58·5	0·2509	0·2435	14·68	14·24

From these numbers the refractive equivalents $P\dfrac{\mu_\alpha-1}{d} = r_\alpha$ and $P\dfrac{A-1}{d} = r_A$ of the following elements may be calculated :—

			r_α.	r_A.
I. Chlorine, calculated from	C Cl⁴	.	9·80	9·55
,,	,, C HCl³	.	9·75	9·48
,,	,, C² H⁴ Cl²	.	9·82	9·57
	Mean . . .		9·79	9·53
			±0·04	±0·04

II. Bromine, calculated from $C^2 H^5$ Br . 14·96   14·40

    ,,   ,, $C^5 H^{11}$ Br . 15·68   15·07

    ,,   ,, $C^2 H^4$ Br^2 . 15·39   14·78

    Mean . . . 15·34   14·75

    ±0·36   ±0·34

III. Iodine, calculated from . C H^3 I . 23·99   22·69

    ,,   ,, $C^2 H^5$ I . 24·46   23·10

    ,,   ,, $C^5 H^{11}$ I . 26·16   24·85

    Mean . . . 24·87   23·55

    ±1·08   ±1·08

IV. Sulphur, taking $Cl_a = 9·79$, $\left.\right\}$ C S^2 . . 16·03   14·74
    calculated from . .

    ,,   ,,   S^2 Cl^2 . . 16·03

V. Phosphorus, calculated from PCl^3 . . 14·93   14·60

VI. Arsenic ,, ,, As Cl^3 . . 20·22   18·84

VII. Antimony ,, ,, Sb Cl^5 . . 25·66

VIII. Tin ,, ,, Sn Cl^4 . 19·89   18·64

IX. Silicon ,, ,, Si Cl^4 . 7·90   7·81

X. Sodium ,, ,, Na Cl . 4·89   4·71

The author gives in the following Table the refractive equivalent which he has obtained, and the values for the specific refractive power obtained by dividing the refractive equivalents by the atomic weights. He gives at the same time Schrauf's refractive equivalents, which that physicist calculated from trustworthy observations by various experimenters:—

	P.	$P\dfrac{\mu_a-1}{d}$.	$P\dfrac{A-1}{d}$.	$\dfrac{\mu_a-1}{d}$.	$\dfrac{A-1}{d}$.	Schrauf's refractive equivalent.
Hydrogen	1	1·30	1·29	1·3000	1·2900	1·57
Chlorine.........	35·5	9·79	9·53	0·2758	0·2685	8·58
Bromine.........	80	15·34	14·75	0·1918	0·1844	13·85
Iodine...........	127	24·87	23·55	0·1958	0·1854	23·10
Oxygen	16	3·00	2·90	0·1875	0·1813	3·03
Sulphur	32	16·03	14·74	0·5009	0·4606	16·32
Phosphorus ...	31	14·93	14·60	0·4816	0·4710	18·81
Arsenic	75	20·22	18·84	0·2696	0·2512	14·45
Antimony	122	25·66	......	0·2103		
Carbon	12	5·00	4·86	0·4167	0·4050	4·85
Silicium	28	7·90	7·81	0·2821	0·2789	6·27
Tin...............	118	19·89	18·64	0·1686	0·1580	23·47
Sodium	23	4·89	4·71	0·2126	0·2048	4·54

There is thus seen to be a sufficiently close agreement between the values for the refractive equivalents of those elements which could be calculated from observations in the free state, and the values

deduced by Landolt and the author. This is more particularly the case with H, Cl, Θ, S, and ϴ, while as regards P there is a considerable divergence. Of the refractive equivalents determined by Schrauf from compound bodies, agreement is only met with in the case of Br and I, and to a less extent in Si. As and Sn exhibit marked divergence, which is to be ascribed to the circumstance that Schrauf has calculated the corresponding numbers from arsenic-ethyle and stannethyle, two substances which are difficult to observe and to obtain pure.

LV. *Proceedings of Learned Societies.*

ROYAL SOCIETY.

[Continued from p. 398.]

April 23, 1868.—Dr. William Allen Miller, Treasurer and Vice-President, in the Chair.

THE following communications were read:—

"New Researches on the Dispersion of the Optic Axes in Harmotome and Wöhlerite, proving these Minerals to belong to the Clinorhombic (Oblique) System." By M. A. L. O. Des Cloiseaux.

We are already acquainted with a considerable number of crystals, natural as well as artificial, the forms of which have only been determined with precision by the examination of their optical properties as doubly refracting bodies. Harmotome and Wöhlerite furnish two fresh examples of this; and they afford all the more important proof of the necessity of appealing to these properties, inasmuch as the crystals of these substances would appear certainly to be derived from a right rhombic prism, so long as we consider only the apparent symmetry of their external forms, or the orientation of the plane containing their optic axes. The different sorts of dispersion which these axes might be capable of presenting are so feeble, and so difficult of appreciation on account of the slight transparency of Wöhlerite, and the complex structure of the crystals of Harmotome, that the determination of these dispersions has hitherto been too incomplete to allow of any conclusion being drawn as to the crystalline type they might otherwise serve to characterize.

It was a remark of M. Axel Gadolin that induced the author to resume the attentive study of the phenomena of dispersion, first in Harmotome, and then in Wöhlerite, and as a consequence to modify the crystallographic type to which these minerals have been in general referred.

Harmotome.

Several years ago the author showed that simple crystals of Harmotome did not exist, and that those of Strontian in Scotland (Morve-

nite), considered as such, presented, in fact, a twinning formed by the interpenetration of two principal individuals. The particular orientation of the plane of the optic axes in each of the crystals of which the least complicated of such groups are composed had led him to refer their crystalline form to a right rhombic prism of 124° 47′; and he had been induced to look on this prism as presenting a peculiar sort of hemihedrism, or rather hemimorphism, such that only one-half of the fundamental rhombic octahedron existed—that, namely, formed of four faces parallel two and two, and lying in the same zone. More recently, in studying the modifications which heat induces in the position of the optic axes and of their plane, he observed a phenomenon less compatible with the hypothesis of a primitive rhombic form ; but the slight transparency of the plates on which he operated, the wide separation of the optic axes, which rendered the examination of the two systems of rings almost impossible in air, and, finally, the almost complete absence of dispersion led him to regard the observed result as an apparent anomaly, attributable to the highly complex structure of the crystals.

Desirous of verifying the truth of a suggestion communicated to him by M. Gadolin in June 1867, the author had some new plates cut normal to the acute *positive* bisectrix from very transparent crystals of the Scotch Morvenite, and he has been able to establish the existence of a very decided twisted dispersion. In consequence of the smaller mutual inclination of the optic axes in these than in the former plates, the author was also able to satisfy himself directly that the displacement impressed by heat on the plane containing these axes is a rotary one, quite analogous to that which he had shown to exist in borax and Heulandite. It is therefore now beyond doubt that the crystalline type of Harmotome is the oblique rhombic prism ; and the author has corrected the crystallographic description of the mineral accordingly.

Wöhlerite.

In his 'Manual of Mineralogy,' the author had described the crystals of Wöhlerite as derivable from a prism of very nearly 90°. From the point of view from which a consideration of the orientation of their optic axes had induced him to regard them, they appeared to offer a certain number of homohedral forms associated with forms that were hemihedral or hemimorphic, analogous to those that he had drawn attention to in Harmotome. Having proved that the latter mineral belongs to the clinorhombic system, he endeavoured to ascertain whether this was not also the case with Wöhlerite, all the forms of which would in that event be homohedral. But in this case a study of the different varieties of dispersion is rendered difficult by the yellow colour, and by the imperfect transparency presented by the substance even when in very thin plates. Besides this, contrary to what is found in Harmotome, while the dispersion belonging to the optic axes is very distinct, the *horizontal and twisted*

dispersions, which should be sought for in plates normal to the two bisectrices, are, on the contrary, but slightly evident. However, on examining in oil some thin plates placed so as to have the plane of their optic axes horizontal and perpendicular to the plane of polarization, the author observed in the plates normal to the obtuse *positive* bisectrix some faint blue and red fringes, dispersed in contrary directions above and below the bars which traverse the two systems of rings, indicating the existence of an appreciable *twisted* dispersion. In the plates normal to the acute *negative* bisectrix, the transverse bar of each system is bordered on one side by a very pale blue, and on the opposite side by an equally pale yellow, the horizontal dispersion being thus feebly indicated.

The crystals of Wöhlerite ought, then, to be referred to an oblique rhombic prism, in which the plane of symmetry is normal to the plane which contains their optic axes. The primitive form which it seems most convenient to choose is a prism with an angle of very nearly 90°, which presents a cleavage, easy though interrupted, parallel to its plane of symmetry, and cleavages which are more difficult, in the directions of the lateral faces *m* and of the plane *h'*, which is parallel to the horizontal diagonals of the base.

The author then describes in detail the crystalline form of Wöhlerite as thus corrected.

"On the Law of the Resistance of the Air to Rifled Projectiles." By Charles W. Merrifield, F.R.S., Principal of the Royal School of Naval Architecture.

At the beginning of this month Lieut.-Col. H. R. Halford applied to the author to obtain for him the law of atmospheric resistance resulting from his experiments in shooting with Metford's match-rifle, a small-bore with increasing pitch. Col. Halford had determined by experiment the elevations required for the ranges 100, 200, &c. up to 1100 yards, each determination being derived from a very large number of shots; and the table of experimental elevations corresponding to these various ranges formed the datum furnished to the author.

As all the trajectories were very low, the greatest elevation amounting to only 2° 35′ 30″, the author assumed, as a sufficiently close approximation, that the vertical motion was determined solely by the force of gravity, and that the effect of the resistance of the air on the velocity was the same as if the projectile had moved strictly in a horizontal line. Consequently the depression of the point in which the target is struck, below the initial tangent to the path, becomes a measure of the time of flight, according to the usual law of falling bodies; and the mean horizontal velocity being thus known for a series of different ranges, we can calculate the mean velocity for every 100 yards of a long range, and thence determine the resistance.

The author commenced his calculations from an assumed velocity of 1360 feet per second, in accordance with the results obtained at short ranges, and assumed for trial a resistance varying as the square

of the velocity, but found that this law did not fit the results at all. A resistance varying as the cube of the velocity was then tried, and found very nearly to agree with the results of observation ; and the agreement became, we may say, perfect when the assumed initial velocity was slightly corrected.

As the calculations and experiments were all made without any notion of the resulting law, and without any knowledge of the work already done by Professor Hélie and Professor Bashforth, they afford a remarkable confirmation of the results obtained by those gentlemen. This is the more worthy of notice, as their data belong to pieces of large calibre, and the author's to small arms.

April 30.—Lieut.-General Sabine, President, in the Chair.

The following communication was read :—

"The Specific Heat of Mixtures of Alcohol and Water." By A. Dupré, Ph.D., Lecturer on Chemistry at the Westminster Hospital, and F. J. M. Page.

The authors have examined a number of mixtures of alcohol and water. They show that the specific heat of these mixtures, up to an alcoholic strength of about 36 per cent., is higher than the specific heat of water itself.

Two methods were employed for estimating the specific heat, exactly opposite in principle.

The first consisted in heating a metallic weight to a certain temperature in a steam-oven, similar to that employed by Regnault in his researches, and then plunging it into the liquid the specific heat of which was to be estimated. The rise in the temperature of equal quantities of different liquids, produced by the introduction of the same weight heated to the same temperature, is inversely proportional to the specific heat of such liquids.

Two weights and several calorimeters of different sizes were used. One of the weights was made of brass, and weighed 246·49 grms.; the other was of copper, gilt, weighing 614·49 grms. Both weights were made in the form of stout rings ; and in the inner cylindrical opening of each a small fan-wheel was inserted.

These rings, after being heated and let down into the calorimeter, were attached to a strand of worsted, and held freely suspended in the liquid of the calorimeter. The worsted had previously been twisted, and when now allowed to untwist it causes a rapid rotation of the ring. The fan-wheel fixed inside the ring thereby produces a current, which, passing through the ring, not only serves to mix the liquid thoroughly, but also considerably facilitates the rapid cooling of the weight.

The calorimeters, as usual, consisted of cylindrical vessels made of very thin polished brass, supported on stretched silk cords, and surrounded by a double cylinder of tin-plate to prevent, as far as possible, any gain or loss by radiation.

The temperature of the liquid was taken by a small thermometer, having a bulb 60 millims. long and about 2·5 millims. diameter. Each degree was divided into twenty parts; and by means of a telescope $\frac{1}{200}$ of a degree could be read off.

The authors give experiments which prove that the high specific heats observed are not due to evaporation caused by the introduction of the heated metals into the calorimeter.

The second method used was that generally employed. A certain weight of the liquid, the specific heat of which is to be estimated, enclosed in a suitable vessel, is heated and then plunged, vessel and all, into a calorimeter containing a known weight of distilled water. The temperature of the calorimeter will rise, owing to the introduction of the heated liquid; and the elevations in temperature produced by different liquids will, in this case, be directly proportional to their specific heats.

The following Tables give the means of the various results obtained.

Four series of experiments were made. In the first series the brass weight was employed; it was heated to a temperature of about 98° C. In the second and third series the copper weight was used, heated to about 98° and 42° C. respectively. The fourth series was conducted in the ordinary manner.

Specific heat of

5 per cent. spirit	Series II.	101·5
10 per cent. spirit	Series I. 103·55	
	Series II. 103·49	
	Series III. 103·83	
	Series IV. 103·71	
	Mean	103·64
20 per cent. spirit	Series I. 104·16	
	Series II. 104·27	
	Series IV. 104·49	
	Mean	104·30
30 per cent. spirit	Series II.	102·47
36 per cent. spirit	Series II.	99·90
43 per cent. spirit	Series II.	97·59
83 per cent. spirit	Series II.	65·88

The authors finally draw special attention to the circumstance that the specific heat of these mixtures not only rises in some cases (up to an alcoholic strength of 36 per cent.) above the specific heat of water, but is above the calculated mean specific heat up to an alcoholic strength of about 74–80 per cent.; beyond which it seems slightly below the calculated mean according to the researches of Regnault and Kopp.

The maximum elevation above the calculated mean coincides pretty closely with the point of maximum contraction.

LVI. *Intelligence and Miscellaneous Articles.*

ON THE RELATION WHICH EXISTS BETWEEN THE COHESION OF A
COMPOUND BODY AND THE COHESIONS OF ITS ELEMENTS. BY
M. J. MOUTIER.

M. HIRN has enunciated a general relation which includes the laws
of Boyle and Mariotte and of Gay-Lussac as a particular case.
He has shown[*] that, dividing by the absolute temperature the product
of the interatomic volume into the sum of the internal and external
pressures, a constant number is obtained for the same body, whatever
its physical condition. Thus, if P be the external pressure, R the
internal pressure or the cohesion[†], V the volume of the body, ψ the
invariable volume occupied by the atoms, and T the absolute tempe-
rature, we have

$$\frac{(R+P)(V-\psi)}{T} = \text{constant.}$$

I have endeavoured[‡] to establish, independently of any hypothesis
as to the nature of thermal phenomena, that this constant is equal
to half the product obtained by multiplying the mechanical equiva-
lent of heat E by the quantity of heat necessary for raising the body
through one degree, independently of any external or internal work.
Calling M the weight of the body, K its absolute specific heat inde-
pendently of the physical condition, the preceding relation may then
be written

$$\frac{(R+P)(V-\psi)}{T} = \tfrac{1}{2} MKE,$$

or

$$MK = \frac{2(R+P)(V-\psi)}{TE}.$$

This quantity MK represents the quantity of heat necessary to raise
the body one degree, independently of any external or internal work,
or, if we like, the quantity of heat necessary to raise the temperature
of the atoms through one degree.

Connecting with this relation the law of the absolute specific heats
of compound bodies, we get a relation between the cohesion of a
compound body and the cohesions of its elements at the same tem-
perature.

Suppose that the two bodies A and A′, both under the pressure P
and at the temperature T, combine, forming a body C which we sup-
pose to be under the same conditions of temperature and pressure.
Let R and R′ be the cohesions of the two bodies A and A′, V and
V′ their volumes, ψ and ψ' the invariable volumes occupied by the

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[*] *Exposition Analytique et Expérimentale*, 1865, p. 106.
[†] G. A. Hirn, *Annales de Chimie*, 4th series, vol. xi. p. 90.
[‡] *Comptes Rendus*, vol. lxiv. p. 653.

atoms, ϕ the cohesion of the compound body C, W its volume ; the atomic volume of the compound is moreover $\psi+\psi'$.

The quantities of heat necessary for raising the temperature of the atoms by one degree are respectively in the case of the three bodies:—

$$2\,\frac{(\mathrm{R}+\mathrm{P})(\mathrm{V}-\psi)}{\mathrm{TE}},$$

$$2\,\frac{(\mathrm{R}'+\mathrm{P})(\mathrm{V}'-\psi')}{\mathrm{TE}},$$

$$2\,\frac{(\rho+\mathrm{P})(\mathrm{W}-\psi-\psi')}{\mathrm{TE}}.$$

Now, to heat the atoms in the combination C, the same quantity of heat must be used as if they were free* ; the latter quantity is then equal to the sum of the two former, and after reducing we have the general relation

$$(\rho+\mathrm{P})(\mathrm{W}-\psi-\psi')=(\mathrm{R}+\mathrm{P})(\mathrm{V}-\psi)+(\mathrm{R}'+\mathrm{P})(\mathrm{V}'-\psi').\ .\ \ (1)$$

After an obvious reduction this general relation may be written

$$(\rho+\mathrm{P})\mathrm{W}-\rho(\psi+\psi')=(\mathrm{R}+\mathrm{P})\mathrm{V}-\mathrm{R}\psi+(\mathrm{R}'+\mathrm{P})\mathrm{V}'-\mathrm{R}'\psi'.$$

In the case of gases the cohesions or internal pressures are feeble as compared with the external pressure ; the atomic volumes are also very small as compared with the apparent volumes, and the products $\mathrm{R}\psi$, $\mathrm{R}'\psi'$, $\rho(\psi+\psi')$ may usually be neglected ; and we have then, with a sufficiently close approximation,

$$\rho=\mathrm{R}\,\frac{\mathrm{V}}{\mathrm{W}}+\mathrm{R}'\,\frac{\mathrm{V}'}{\mathrm{W}}+\Big(\frac{\mathrm{V}+\mathrm{V}'}{\mathrm{W}}-1\Big)\mathrm{P}. \qquad (2)$$

If the volumes of two gases which combine are known, as well as the volume of the compound in the state of gas or of vapour, we obtain by means of this relation the cohesion of the compound as a function of the cohesion of the elements and of the external pressure.

This relation gives rise to some remarks.

(1) When two gases combine in equal volumes without condensation,

$$\mathrm{V}=\mathrm{V}'=\tfrac{1}{2}\,\mathrm{W},$$

$$\psi=\tfrac{1}{2}\,(\mathrm{R}+\mathrm{R}').$$

The cohesion of the compound is equal to the arithmetical mean of the cohesions of the elements; it is independent of the external pressure.

Thus the cohesion of binoxide of nitrogen is equal to half the sum of the cohesions of nitrogen and of oxygen. These two permanent gases have very feeble cohesions. The cohesion of binoxide of nitrogen should also be very small ; and this gas is permanent.

In like manner the cohesion of hydrochloric acid is the arithmetical mean of the cohesions of chlorine and of hydrogen. Chlorine,

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* G. A. Hirn, *Exposition Analytique et Expérimentale*, 1865.

which is a gas easily liquefied, has a far greater cohesion than hydrogen : as regards cohesion, hydrochloric acid is between hydrogen and chlorine, and thus it is more difficult to liquefy than chlorine.

(2) When the combination of two gases is accompanied by a condensation, the cohesion of the compound depends on the internal pressure; and as the volume $V + V'$ is then greater than V'', the cohesion in the case of this gas is much greater than in the preceding case.

In like manner, gaseous combinations formed with condensation of the elements are much more easily liquefied than compounds formed without condensation. Thus it is that protoxide of nitrogen, in which the condensation is equal to a third, could be liquefied; while binoxide of nitrogen, formed without condensation, has hitherto resisted liquefaction.

(3) When two compounds C and C_1 corresponding to the same volume W are formed of the same elements A and A', and only differ by the volumes V and V' of one of the elements A, the volume of the second element being supposed invariable, there is a difference between the cohesions ρ and ρ' of the two compounds represented by the relation

$$(\rho' - \rho) = (R + P)\frac{V' - V}{W}.$$

In this case the cohesion increases proportionally to the number of volumes of the element A added to the combination, and proportionally to the cohesion of the element A increased by the external pressure.

Thus carbonic acid and carbonic oxide, with the same volume and under the same conditions of temperature and pressure, contain the same quantity of carbon ; carbonic acid contains more oxygen than carbonic oxide. The cohesion of carbonic acid is greater than that of carbonic oxide; and carbonic acid is the only one of these two gases which has hitherto been liquefied.

Olefiant gas and marsh-gas present another instance.

(4) If in a compound C an element A be replaced by another element A_1 which corresponds to the same volume as A, without the volume W of the compound being modified, the element A' being further supposed to be unchanged, a new compound C_1 is obtained whose cohesion ρ_1 is different from ρ.

If R_1 be the cohesion of the element A_1, we have from formula (2)

$$\rho' - \rho = (R_1 - R)\frac{V}{W}.$$

Thus the difference in the cohesions of the two compounds, C_1 and C, is proportional to the difference of the cohesions in the two elements A_1 and A.

So that, substituting chlorine for hydrogen, bromine for chlorine, iodine for bromine, the compounds obtained by substitution are less volatile.—*Comptes Rendus*, March 23, 1868.

ON SOLAR RADIATION. BY M. SORET.

In prosecuting my researches on the solar heat by the aid of the actinometer which I have briefly described*, I have lately made some observations on the nature of the rays absorbed by the atmosphere.

The intensity was measured either by allowing the rays to fall directly on the thermometer of the actinometer, or by first causing them to pass through a layer of distilled water of about 5 centims. thickness. This water was contained in a brass tube closed by two glass plates.

If T be the increase in temperature in the first case, and t the increase in the second case, the ratio $\dfrac{t}{T}$ will be greater the greater is the proportion of rays not absorbed by the tube with water†. Now water, like glass, allows luminous heat to pass freely, but absorbs in great part obscure heat, and especially the least-refrangible rays. Hence, making these observations for different heights of the sun above the horizon (that is, for different thicknesses of the atmospheric layer traversed by the rays), indications will be obtained as to the nature of the heat arrested by the atmosphere.

The absolute values of T and t for the same solar height vary with atmospheric conditions, such as the transparency and the moisture of the air. Hence, to appreciate the influence of an increase in the atmospheric thickness, the values of $\dfrac{t}{T}$ should be compared which are obtained at different times of the same day. It will be seen that this ratio is greater in the middle of the day than when the sun is at a small height above the horizon.

The following are some observations made at Geneva :—

Date.	Time.	T.	t.	$\dfrac{t}{T}$.
	h m	°	°	
Feb. 27.	1 45	14·19	8·25	0·581
,, 27.	4 25	9·07	5·31	0·545
March 9.	12 30	14·58	8·66	0·594
,, 9.	5 10	7·81	3·66	0·469
,, 13.	11 30	14·70	8·35	0·568
,, 13.	4 46	10·78	5·77	0·535
,, 13.	5 20	7·06	3·41	0·484
,, 14.	7 10	7·04	3·04	0·432
,, 14.	12 24	14·85	8·51	0·572
,, 14.	5 30	6·74	3·37	0·500
April 3.	12 36	13·89	8·27	0·596
,, 3.	5 36	7·51	3·37	0·449

* Phil. Mag. S. 4. vol. xxxiv. p. 404.

† In order that t may exactly give the amount of heat not absorbed by the tube full of water, a correction should be introduced for the heat reflected at the limits of the media ; but as this correction is proportional to the quantity of heat transmitted, it would not modify the conclusions to be drawn from the results cited below.

A series of observations made on the 1st of April on Mont Solère, at a height of about 1250 metres, gave me the following values of the ratio $\frac{t}{T}$:—

Time.	$\frac{t}{T}$.	Time.	$\frac{t}{T}$.
h m		h m	
2 4	0·577	5 26	0·566
2 16	0·578	5 38	0·531
2 34	0·597	5 50	0·528

The value of $\frac{t}{T}$, especially when the sun is near the horizon, appeared greater at Geneva; but it would be premature to deduce from the observation of a single day a general conclusion on the influence of latitude.

Substituting for the water in the tube a solution of alum, I aptained (at Geneva, the 21st of March) the following results, which approximate closely to those given above:—

Time.	$\frac{t}{T}$.	Time.	$\frac{t}{T}$.
h m		h m	
7 18	0·397	9 16	0·557
7 30	0·462	12 28	0·588
7 42	0·486	5 30	0·458

It follows from these observations that, in the conditions under which I worked, the atmosphere stops the luminous rays in greater proportion than the obscure rays which are absorbed by water. There is an obvious analogy between this result and the well-known property of the atmosphere, of allowing the red rays to pass more easily than the more refrangible rays.

It will be observed that the above experiments were made in cold and dry weather. It will be interesting to ascertain whether the same result holds when the tension of vapour is more considerable. —*Comptes Rendus*, April 20, 1868.

ON THE INTERNAL WORK OF GASES.   BY M. A. CAZIN.

I have made observations on the variations of pressure in a gaseous mass which has suddenly passed from one reservoir into another, from the moment at which the pressure began to be equal to the time that the gas had assumed its original temperature.

The following is the principle of the method of observation. The gas is at the outset under the same pressure in the two reservoirs, which are then connected with a sulphuric-acid manometer, and the level noted. A valve is closed, which cuts off communication between the reservoirs and the manometer. By means of a pump, part of the gas is driven from one reservoir into the other. A large stopcock between the reservoirs being opened; sudden expansion takes place, and the motion of the stopcock opens in turn the valve of the manometer. The apparatus indicates the time when the expansion commences, and at which the valve has been opened; and the level in the manometer at known intervals is then observed.

For this purpose a voltaic circuit is used containing an electromagnet the armature of which is provided with a pencil; against this pencil a band of paper is uncoiled with known velocity. The stopcock in turning closes the circuit as soon as the expansion commences, and then opens it at the same time as the valve; the circuit, finally, is closed for a moment each time the manometer is read off. From the marks left on the paper the necessary times are easily known.

Let H be the difference of level observed at different times, H' the final difference observed when the gas has resumed its original temperature; a curve is traced having for ordinates the values H' and H, and for abscissæ the times calculated from the moment the expansion commenced.

By gradually increasing the time which elapses between the commencement of the expansion and the opening of the valve, leaving other circumstances unaltered, a series of curves is obtained which succeed each other regularly, and a comparison of which gives the curve of real pressure which the gas possesses at various intervals. By this device we avoid being compelled to attempt the impossibility of having a manometer which shall instantaneously indicate the varying pressure of the gas.

This method is analogous to that which I used in 1862, in an investigation on the expansion and compression of gases. Ordinarily changes of bodies are observed by means of an instrument in which a moveable part indicates almost instantaneously the condition of the body. When the change is very rapid, the moveable part is always behindhand, and the displacements observed cannot directly lead to a knowledge of the change in question. But if the degree of retardation be varied, and if the law of the displacement be represented in each experiment by a curve, the law of the change may be deduced from a great number of such curves. In this manner phenomena so fugitive as the movements of a gaseous mass become accessible to observation. I have used a reservoir of 9 litres containing gas under about 4 atmospheres, and a reservoir of 34 or of 60 litres containing highly rarefied gas. The stopcock which separated the two reservoirs had a conduit of 4 centims. diameter.

The general result of the experiments is as follows:—As soon as the two reservoirs are connected, the pressure becomes equal in a

time less than 0·1 second; the pressure increases then for several seconds, at first rather rapidly, but then more slowly, and the more so the greater the divergence of the gas from Mariotte's law. The pressure attains a maximum, and then very slowly decreases until the initial temperature is set up.

This result is easily explained on thermodynamic principles. The moment inequality of pressure begins to be set up, part of the gas eddies about; there has been a lowering of temperature in the expanded part, an increase in the compressed part. The *vis viva* of the part in motion is gradually converted into heat, and consequently the pressure increases. If the sides were impervious to heat, equilibrium would be established without any external work being brought into play, or any heat taken from or given to the surrounding bodies. The temperature would then be lower than the original temperature; and the difference would be greater the greater the divergence from Mariotte's law. But the sides impart heat to the cold part of the gaseous mass, and take it, on the contrary, from the heated part, without there being an exact compensation between the two effects. The final result is that the mass receives a little heat from without; hence, when a mixture of all the gases is effected, the temperature is a little higher than the original temperature, which it only acquires after a tolerably long time.

These observations complete a celebrated experiment in which Mr. Joule investigated the ultimate thermal condition of a gas which had expanded without external work. This effect, which it is almost impossible to observe in the water surrounding the reservoirs, is clearly manifested in my experiments. Without the necessity of a very great pressure, they furnish an undoubted proof of the spontaneous cooling which a gaseous mass undergoes, and exhibit various accessory circumstances. We know that this cooling indicates the existence of a molecular attraction in gases, and that the corresponding loss of heat is equal to the production of a certain quantity of internal work. The calculation of this amount of work under given conditions is an interesting application of thermodynamic formulæ.

Treating a series of problems on this question, I have rediscovered the principal circumstances observed in my experiments. I have made a numerical calculation for carbonic acid, using an empirical formula which connects the pressure, the volume, and the temperature. This formula was enunciated by Mr. Rankine; and Mr. Joule and Sir W. Thomson used it in their researches on the issue of gases through small apertures. I have merely changed the constants of this formula, so that it might satisfy the experimental data of M. Regnault relative to the compressibility and expansion of carbonic acid gas.—*Comptes Rendus*, March 9, 1868.

INDEX to VOL. XXXV.

END OF THE THIRTY-FIFTH VOLUME.

ALERE   FLAMMAM.

CONTENTS of N° 234.—*Fourth Series.*

GEOLOGY.—KING'S COLLEGE, LONDON.—PROFESSOR TENNANT, F.G.S., commenced a Course of LECTURES on GEOLOGY on *Friday*, *January* 24, 1868, at 9 A.M. They will be continued on each succeeding Wednesday and Friday at the same hour. A shorter Course will be given on Thursday evenings, from 8 to 9. First Lecture, January 23. Text-book, Lyell's 'Elements of Geology.' Mr. TENNANT accompanies his Students to the Public Museums and to places of Geological interest in the country. The Lectures on MINERALOGY begin in October and terminate at Christmas.

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FOURTH SERIES.

Nº 236.—MARCH 1868.

GEOLOGY.—KING'S COLLEGE, LONDON.—PROFESSOR

TENNANT, F.G.S., commenced a Course of LECTURES on GEOLOGY on *Friday, January* 24, 1868, at 9 A.M. They will be continued on each succeeding Wednesday and Friday at the same hour. A shorter Course will be given on Thursday evenings, from 8 to 9. First Lecture, January 23. Text-book, Lyell's 'Elements of Geology.' Mr. TENNANT accompanies his Students to the Public Museums and to places of Geological interest in the country. The Lectures on MINERALOGY begin in October and terminate at Christmas.

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