Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

On the Physics of Media that are Composed of Free and Perfectly Elastic Molecules in a State of Motion

J. J. Waterston and Lord Rayleigh

Phil. Trans. R. Soc. Lond. A 1892 **183**, doi: 10.1098/rsta.1892.0001, published 1 January 1892

Email alerting service Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click **here**

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to: **http://rsta.royalsocietypublishing.org/subscriptions**

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

PHILOSOPHICAL TRANSACTIONS.

I. *On the Physics of Media that are Composed of Free and Perfectly Elastic Molecules in a State of Motion.*

By J. J. WATERSTON.

Communicated by Captain BEAUFORT, *R.N., F.R.S., &c.*

Received December 11, 1845,—Read March 5, 1846.

[PLATES 1, 2.]

Introduction by Lord RAYLEIGH, *Sec.R.S.*

THE publication of this paper after nearly half a century demands a word of explanation; and the opportunity may be taken to point out in what respects the received theory of gases had been anticipated by WATERSTON, and to offer some suggestions as to the origin of certain errors and deficiencies in his views.

So far as I am aware, the paper, though always accessible in the Archives of the Royal Society, has remained absolutely unnoticed. Most unfortunately the abstract printed at the time ('Roy. Soc. Proc.,' 1846, vol. 5, p. 604; here reprinted as Appendix I.), gave no adequate idea of the scope of the memoir, and still less of the nature of the results arrived at. The deficiency was in some degree supplied by a short account in the 'Report of the British Association' for 1851 (here reprinted as Appendix II.), where is distinctly stated the law, which was afterwards to become so famous, of the equality of the kinetic energies of different molecules at the same temperature.

My own attention was attracted in the first instance to WATERSTON'S work upon the connection between molecular forces and the latent heat of evaporation, and thence to a paper in the 'Philosophical Magazine' for 1858, "On the Theory of Sound." He there alludes to the theory of gases under consideration as having been started by HERAPATH in 1821, and he proceeds:—

"Mr. HERAPATH unfortunately assumed heat or temperature to be represented by

The Royal Society is collaborating with JSTOR to digitize, preserve, and extend access to *Philosophical Transactions of the Royal Society of London. A.* www.jstor.org

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

the simple ratio of the velocity instead of the square of the velocity—being in this apparently led astray by the definition of motion generally received—and thus was baffled in his attempts to reconcile his theory with observation. If we make this change in Mr. HERAPATH's definition of heat or temperature, viz., that it is proportional to the *vis viva*, or square velocity of the moving particle, not to the momentum, or simple ratio of the velocity, we can without much difficulty deduce, not only the primary laws of elastic fluids, but also the other physical properties of gases enumerated above in the third objection to NEWTON's hypothesis. In the Archives of the Royal Society for 1845–1846, there is a paper "On the Physics of Media that consists of perfectly Elastic Molecules in a State of Motion," which contains the synthetical reasoning upon which the demonstration of these matters rests. The velocity of sound is therein deduced to be equal to the velocity acquired in falling through three-fourths of a uniform atmosphere. This theory does not take account of the size of the molecules. It assumes that no time is lost at the impact, and that if the impacts produce rotatory motion, the *vis viva* thus invested bears a constant ratio to the rectilineal *vis viva*, so as not to require separate consideration. It also does not take account of the probable internal motion of composite molecules; yet the results so closely accord with observation in every part of the subject as to leave no doubt that Mr. HERAPATH's idea of the physical constitution of gases approximates closely to the truth. M. KRÖNIG appears to have entered upon the subject in an independent manner, and arrives at the same result; M. CLAUSIUS, too, as we learn from his paper "On the Nature of the Motion we call Heat" ('Phil. Mag.,' vol. 14, 1857, p. 108)."

Impressed with the above passage and with the general ingenuity and soundness of WATERSTON's views, I took the first opportunity of consulting the Archives, and saw at once that the memoir justified the large claims made for it, and that it marks an immense advance in the direction of the now generally received theory. The omission to publish it at the time was a misfortune, which probably retarded the development of the subject by ten or fifteen years. It is singular that WATERSTON appears to have advanced no claim for subsequent publication, whether in the Transactions of the Society, or through some other channel. At any time since 1860 reference would naturally have been made to MAXWELL, and it cannot be doubted that he would have at once recommended that everything possible should be done to atone for the original failure of appreciation.

It is difficult to put oneself in imagination into the position of the reader of 1845, and one can understand that the substance of the memoir should have appeared speculative and that its mathematical style should have failed to attract. But it is startling to find a referee expressing the opinion that "the paper is nothing but nonsense, unfit even for reading before the Society." Another remarks "that the whole investigation is confessedly founded on a principle entirely hypothetical, from which it is the object to deduce a mathematical representation of the phenomena of elastic media. It exhibits much skill and many remarkable accordances with the

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

general facts, as well as numerical values furnished by observation. . . . The original principle itself involves an assumption which seems to me very difficult to admit, and by no means a satisfactory basis for a mathematical theory, viz., that the elasticity of a medium is to be measured by supposing its molecules in vertical motion, and making a succession of impacts against an elastic gravitating plane." These remarks are not here quoted with the idea of reflecting upon the judgment of the referee, who was one of the best qualified authorities of the day, and evidently devoted to a most difficult task his careful attention; but rather with the view of throwing light upon the attitude then assumed by men of science in regard to this question, and in order to point a moral. The history of this paper suggests that highly speculative investigations, especially by an unknown author, are best brought before the world through some other channel than a scientific society, which naturally hesitates to admit into its printed records matter of uncertain value. Perhaps one may go further and say that a young author who believes himself capable of great things would usually do well to secure the favourable recognition of the scientific world by work whose scope is limited, and whose value is easily judged, before embarking upon higher flights.

One circumstance which may have told unfavourably upon the reception of WATERSTON's paper is that he mentions no predecessors. Had he put forward his investigation as a development of the theory of D. BERNOULLI, a referee might have hesitated to call it nonsense. It is probable, however, that WATERSTON was unacquainted with BERNOULLI's work, and doubtful whether at that time he knew that HERAPATH had to some extent foreshadowed similar views.

At the present time the interest of WATERSTON's paper can, of course, be little more than historical. What strikes one most is the marvellous courage with which he attacked questions, some of which even now present serious difficulties. To say that he was not always successful is only to deny his claim to rank among the very foremost theorists of all ages. The character of the advance to be dated from this paper will be at once understood when it is realised that WATERSTON was the first to introduce into the theory the conception that heat and temperature are to be measured by *vis viva*. This enabled him at a stroke to complete BERNOULLI's explanation of pressure by showing the accordance of the hypothetical medium with the law of DALTON and GAY-LUSSAC. In the second section the great feature is the statement (VII.), that "in mixed media the mean square molecular velocity is inversely proportional to the specific weight of the molecules." The proof which WATERSTON gave is doubtless not satisfactory; but the same may be said of that advanced by MAXWELL fifteen years later. The law of AVOGADRO follows at once, as well as that of GRAHAM relative to diffusion. Since the law of equal energies was actually published in 1851, there can be no hesitation, I think, in attaching WATERSTON's name to it. The attainment of correct results in the third section, dealing with adiabatic expansion, was only prevented by a slip of calculation.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

In a few important respects WATERSTON stopped short. There is no indication, so far as I can see, that he recognised any other form of motion, or energy, than the translatory motion, though this is sometimes spoken of as vibratory. In this matter the priority in a wider view rests with CLAUSIUS. According to WATERSTON the ratio of specific heats should be (as for mercury vapour) 1·67 in all cases. Again, although he was well aware that the molecular velocity cannot be constant, there is no anticipation of the law of distribution of velocities established by MAXWELL.

A large part of the paper deals with chemistry, and shows that his views upon that subject also were much in advance of those generally held at the time.

The following extract from a letter by Professor MCLEOD will put the reader into possession of the main facts of the case:—

"It seems a misfortune that the paper was not printed when it was written, for it shadows forth many of the ideas of modern chemistry which have been adopted since 1845, and it might have been the means of hastening their reception by chemists.

"The author compares the masses of equal volumes of gaseous and volatile elements and compounds, and taking the mass of a unit volume of hydrogen as unity, he regards the masses of the same volume of other volatile bodies as representing their molecular weight, and in the case of the elements he employs their symbols to indicate the molecules.

"In water he considers that the molecule of hydrogen is combined with half a molecule of oxygen, forming one of steam, and he therefore represents the compound as $HO_{\frac{1}{2}}$. He does not make use of the term "atom" (although he speaks of atomic weight on p. 18, but thinks it divisible), and if he had called the smallest proportion of an element which enters into combination an atom, he would probably have been led to believe that the molecules of some of the simple bodies contain two atoms, and he might have adopted two volumes to represent the molecule, as is done at the present time. The author calls one volume or molecule of chlorine Cl, one volume or molecule of hydrogen H, and one volume or molecule of hydrochloric acid $H_{\frac{1}{2}}Cl_{\frac{1}{2}}$. If he had regarded the molecules as containing two indivisible atoms, these bodies would have been represented, as now, by the formulæ Cl_2, H_2, and HCl respectively, all occupying two volumes. § 15 shows how near he was to this conception. GERHARDT in the Fourth Part of his 'Traité de Chimie Organique,' published in 1856, points out the uniformity introduced into chemical theory by the adoption of this system.

"For carbon he makes C = 12, as now accepted, although I do not find how he arrives at this number. He seems to have anticipated one of RAMSAY'S recent discoveries, that nitrous anhydride (hyponitrous acid, $ON_{\frac{2}{3}}$, No. 26 in the table) dissociates on evaporation into nitric oxide (binoxide of nitrogen, No. 23) and nitric peroxide (nitrous acid, No. 25).

"The values for the symbols for sulphur, phosphorus, and arsenic taken from the vapour densities (and which are multiples of what are believed to be the true atomic weights), cause some complexity in the formulæ of their compounds.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

"There seem to be errors in the formulæ of alcohol and ether on p. 49, for they do not agree with those in the table. They ought probably to be written

$$2\,(HC_{\frac{1}{2}}) + O_{\frac{1}{2}}2H_{\frac{1}{2}} \text{ and } 4\,(HC_{\frac{1}{2}}) + O_{\frac{1}{2}}2H_{\frac{1}{2}}.$$

"Considering how nearly WATERSTON approached what is now believed to be the true theory, it is disappointing to read his controversy with ODLING in 1863 and 1864 ('Phil. Mag.,' vols. 26 and 27), where he seems to oppose the new formulæ then being introduced. He is very dogmatic about the constitution of hydrate of potash: he very properly insists that we can only obtain a knowledge of the molecular weight of bodies that can be volatilized, and of which the vapour densities can be determined, but he does not see the analogy between the hydrate and oxide of potassium with alcohol and ether, probably because he regards these latter bodies as combinations of water with different quantities of olefiant gas. He writes water $HO_{\frac{1}{2}} = 9$, alcohol $CH_2HO_{\frac{1}{2}} = 23$, and ether $C_2H_4 . HO_{\frac{1}{2}} = 37$, whilst he considers potassic hydrate $KO_{\frac{1}{2}} . HO_{\frac{1}{2}} = 56$, and oxide of potassium $KO_{\frac{1}{2}} = 47$, the hydrate having a higher molecular weight than the oxide. If we regard these compounds as derived from water by the replacement of hydrogen by ethyl and potassium respectively, the analogy between the two series is complete (ethyl was discovered in 1849 and is mentioned by WATERSTON).

$H_2O = 18$	$H_2O = 18.$
$(C_2H_5)\,HO = 46$	$KHO = 56.$
$(C_2H_5)_2\,O = 74$	$K_2O = 94.$

"From a remark in the 'Phil. Mag.' (vol. 26, p. 520), I imagined that WATERSTON had arrived at the double atomic weights of many of the metals now adopted, for he gives that of iron as 56 and that of aluminium as 27 calculated from their specific heats, but there is an error in his arithmetic, for 3·3 divided by the specific heat of iron ·1138 gives 28·998, and 3·3 divided by the specific heat of aluminium ·2143 gives 15·399."

With the exception of some corrections relating merely to stops and spelling the paper is here reproduced exactly as it stands in the author's manuscript.—Dec. 1891.

[*Author's Introduction.*]

OF the physical theories of heat that have claimed attention since the time of BACON, that which ascribes its cause to the intense vibrations of the elementary parts of bodies has received a considerable accession of probability from the recent experiments of FORBES and MELLONI. It is admitted that these have been the means of demonstrating that the mode of its radiation is identical with that of light in the quantities of refraction and polarization. The evidence that has been accumulated in favour of the undulatory theory of light has thus been made to support with a great

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

portion of its weight a like theory of the phenomena of heat; and we are, perhaps, justified in expecting that the complete development of this theory will have a much more important influence on the progress of science, because of its more obvious connection and intimate blending with almost every appearance of Nature. Heat is not only the subject of direct sensation and the vivifier of organic life, but it is manifested as the accompaniment of mechanical force. It is related to it both as cause and effect, and submits itself readily to measurement by means of the mechanical changes that are among the most prominent indications of its change of intensity. The undulatory theory at once leads us to the conclusion that, inasmuch as the temperature of a body is a persistent quality due to the motion of its molecules, its internal constitution must admit of it retaining a vast amount of living force. Indeed, it seems to be almost impossible now to escape from the inference that heat is essentially molecular *vis viva*. In solids, the molecular oscillations may be viewed as being restrained by the intense forces of aggregation. In vapours and gases these seem to be overcome; vibrations can no longer be produced by the inherent *vis insita* of the molecules struggling with attractive and repellant forces; the struggle is over and the molecules are free; but they, nevertheless, continue to maintain a certain temperature; they are capable of heating and being heated; they are endowed with the quality heat, which, being of itself motion, compels us to infer that a molecule in motion without any force to restrain or qualify it, is in every respect to be considered as a free projectile. Allow such free projectiles to be endowed with perfect elasticity, and likewise extend the same property to the elementary parts of all bodies that they strike against, and we immediately introduce the principle of the conservation of *vis viva* to regulate the general effects of their fortuitous encounters. Whether gases do consist of such minute elastic projectiles or not, it seems worth while to enquire into the physical attributes of media so constituted, and to see what analogy they bear to the elegant and symmetrical laws of aeriform bodies.

Some years ago I made an attempt to do so, proceeding synthetically from this fundamental hypothesis, and have lately obtained demonstration of one or two points where the proof was then deficient. The results have appeared so encouraging, although derived from very humble applications of mathematics, that I have been led to hope a popular account of the train of reasoning may not prove unacceptable to the Royal Society.—Sept. 1, 1845.

Section I.—Of a Homogeneous Medium and the Laws of its Elasticity.

§ 1. The term medium is, perhaps, not quite appropriate to what is here intended to be signified. We speak of a resisting medium, of the medium of light, and in each expression something is referred to as intervening between bodies, and it is the quality of interposition that entitles it to the name. Here, for want of better, it is employed to denote a certain hypothetical condition of matter which it is the object of this Paper to show has physical properties that resemble those that have been

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

found to belong to aeriform bodies. Inasmuch, therefore, as the word may be applied to a simple unmixed gas so as to speak of it as an oxygen medium or a hydrogen medium, &c., so far we may be allowed the use of it in treating of a hypothetical medium, which we have carefully to refrain from assimilating to any known form of matter until, by synthetical reasoning, circumstantial evidence has been accumulated sufficient to prove or render probable its identity.

To have a proper conception of what the medium is that forms the subject of speculation, we must imagine a vast multitude of small particles of matter, perfectly alike in every respect, perfectly elastic as glass or ivory—but of size, form and texture that requires not to be specified further than that they are not liable to change by mutual action—to be enclosed by elastic walls or surfaces in a space so much greater than their aggregate bulk as to allow them freely to move amongst each other in every direction. As all consideration of attractive forces is left out at present, it is obvious that each particle must proceed on a straight line until it strikes against another, or against the sides of the enclosure; that it must then be reflected and driven into another line of motion, traversing backwards and forwards in every direction, so that the intestine condition of the multitude of these that form the medium may be likened to the familiar appearance of a swarm of gnats in a sunbeam.

The quality of perfect elasticity being common to all the particles, the original amount of *vis viva*, or living, acting force, of the whole multitude must for ever remain the same. If undisturbed by external action it cannot, of itself, diminish or increase, but must for ever remain as unchanged as the matter that is associated with it and that it endows with activity. Such is the case if we view the whole mass of moving particles as one object, but each individual of the multitude must at every encounter give or receive, according to the ever-changing angle and plane of impact, some portion of its force, so that, considered separately, they are for ever continually changing the velocity and direction of their individual motions; striking against and rebounding from each other, they run rapidly in their zig-zag conflict through every possible mode of concurrence, and *at each point of the medium we may thus conceive that particles are moving in every possible direction and encountering each other in every possible manner during so small an elapsed interval of time that it may be viewed as infinitesimal in respect to any sensible period.* The medium must in this way become endowed with a permanent state of elastic energy or disposition to expand, uniformly sustained in every part and communicating to it the physical character of an elastic fluid.

The simplicity of this hypothesis facilitates the application of mathematics in ascertaining the nature and properties of such media, and the study acquires much interest from the analogies that it unfolds. For if the reasoning is correct, the physical laws common to all gases and vapours—those laws, namely, that concern heat and pressure—do actually belong to such media, and may be synthetically deduced from the constitution which has now been assigned to them.

The characteristic which renders a medium susceptible of mathematical treatment is

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

that of its being composed of particles perfectly alike in every respect, but it is chiefly their identity in weight or mass that is the important point of distinction. A particle thus conforms to the definition that the eminent physicist AMPÈRE has given to the term molecule, which we may therefore adopt as a more significant name for the element of a medium.

The first department of the subject must naturally be devoted to the consideration of the circumstances that determine the equilibrium of such a homogeneous medium considered by itself. Its density, by which is to be understood not its specific gravity but the number of molecules in a constant volume,* may be supposed to vary without disturbing its homogeneity. The mean square velocity of the molecules (which in any infinitesimal portion of the medium may be assumed as uniform) we also have to consider as a variable quantity, and the physical qualities of a medium being dependent on these two elements of its constitution, it is necessary to determine clearly their mathematical relations.

§ 2. It is evident from the definition of the hypothesis, that the medium must exert some expansive force on the surface that encloses it; but the nature of the force is not strictly continuous, it is composed of a multitude of successive strokes. Nevertheless, their succession is certainly continuous, and it is not difficult to conceive how they may be sufficient to counterbalance and support a superincumbent weight. To obtain an exact idea of this, let us suppose that a small elastic plane whose weight is n times that of a molecule, is supported by a regular succession of such molecules striking its centre of gravity with a velocity v. We seek to know the condition of their mutual action when an equilibrium is maintained.

The following are the well-known equations that express the law of elastic collision. They are necessarily the foundation of all reasoning on the effects of the mutual action of elastic bodies by impact.

1. *The Meeting Impact.*

Two molecules, B and D, meet directly in an intermediate point and strike each other with the respective velocities β and δ. The velocities after impact are respectively :—

$$\beta_0 = -\beta + \frac{2(\delta+\beta)\mathrm{D}}{(\mathrm{B}+\mathrm{D})}; \quad \text{and} \quad \delta_0 = \delta - \frac{2(\delta+\beta)\mathrm{B}}{(\mathrm{B}+\mathrm{D})};$$

the direction of D's motion being reckoned positive.

2. *The Overtaking Impact.*

The two molecules, B and D, with the same velocities, β and δ, move in the same direction and D overtakes B; the velocities after impact are respectively :—

$$\beta_1 = \beta + \frac{2(\delta-\beta)\mathrm{D}}{(\mathrm{B}+\mathrm{D})}; \quad \text{and} \quad \delta_1 = \delta - \frac{2(\delta-\beta)\mathrm{B}}{(\mathrm{B}+\mathrm{D})};$$

the direction of D's motion being reckoned positive.

* [Attention should be directed to this use of the word "density."—R.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

In the first of these let $\beta_0 = \beta$, $\delta = v$, $B = nD$; then shall

$$\beta = -\beta + \frac{2(v+\beta)}{n+1}; \quad \text{or} \quad \beta = \frac{v}{n},^*$$

which evidently expresses the upward velocity given to the plane by the impulse of one molecule when the velocity of incidence and reflexion is the same. The plane ascends and descends the height due to this velocity, and then encounters the next in the succession of molecular impacts without any transference of force taking place between them; and n being taken an indefinitely great number, β is infinitesimal in respect to v, and the height through which the plane traverses is also infinitesimal, so that it is supported as if by a continuous force of upward pressure. The time between each impact is, according to the law of falling bodies, equal to the time taken by the force of gravity to destroy and reproduce the infinitesimal velocity v/n. This is $2v/gn$: the velocity which a free body gains or loses in a unit of time by the force of gravity being represented by g. The number of impacts in a unit of time is therefore $gn/2v = A$. This, then, is the relation between the weight of the plane, in terms of that of the molecule unity, and the rapidity of the succession of impacts necessary to support it in a condition of statical equilibrium. Now, if the plane forms part of the surface that encloses the medium and that counterbalances by its weight the effect of the impacts of the confined molecules, such effect must correspond with the succession represented by A; and we deduce that *the elastic force of a medium, as represented by the weight or pressure required to confine it, is directly proportional to he number of molecular impacts that take place against a unit surface in a unit time with a constant velocity* (or $e \doteqdot A$, if v is constant) . . . . . I.

§ 3. Such being the nature of the elastic force, it will not be difficult to prove that it increases exactly as the density of the medium. The proposition stands thus: if the number of molecules in a volume of the medium be doubled, the number of impacts that take place on a constant surface in a constant time will also be doubled, the velocity being unchanged.

Suppose the number octupled, the mean distance is reduced to one-half. If they were equidistant and moving in one direction with the constant velocity, it is evident that eight times the previous number would pass the same imaginary plane in the same time, and if the plane were solid that eight times the previous number would impinge against it. Now, although all do not move in one direction, yet in both cases the same proportion of the whole must in each case do so. Whatever may be the density no preference can be assigned to one direction more than to another in the molecular movements; they must in every case be equally distributed in every

* [The case is that where the particle (mass 1) and the plane (mass n) both reverse their velocities at impact. The conservation of *vis viva* is thereby secured, and the condition of momentum gives at once $n\beta = v$.—R.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

direction, and if the number is increased eight times in any one direction it must be so in every other.

This may be viewed in another light. Suppose in both cases, the density being 1 and 8 respectively, that the molecules are arrested in their motion. It is evident that opposite a unit of surface in density 8 there will, in the first row, be four times as many molecules as in density 1, and that the average distance between the rows is only one-half. Suppose the molecules to resume their motion, and compare density 8 with density 1, it is obvious that in half the time four times the number will impinge on the unit of surface, and in the same time eight times the number. Now it has been shown (§ 2) that the elastic force is proportional to the number of molecular impacts made with a constant velocity against a unit of surface in a unit of time, hence we deduce that *the elastic force* (e) *of a medium with a constant mean molecular velocity* (v) *is proportional to its density* (Δ^3) (or $e \doteqdot \Delta^3$, if v or v^2 is constant). . II.

§ 4. Hitherto the molecular velocity has been supposed constant. We have now to enquire how the elasticity of the medium is affected by a change in the velocity from v to mv. The intestine action of the medium may be viewed as the traversing of a certain mean distance, L, by the molecules in a given time, t; and in this time a certain mean number, A, of impacts take place against a unit of surface. If the velocity is increased m times, the distance L is traversed in $1/m$th the time t, or t/m, and in this reduced time the same number of impacts must take place as before took place in the time t; for there is nothing in the change of velocity simply that can alter the ratio that subsists between the mean distance traversed and the mean number of impacts, unless that ratio were subject to change without any change whatever in the medium, which is absurd; hence, in the original time, t, there is m times the original number of impacts, A.

It was shown in § 2 that if the weight of each of the molecules were represented by 1, their mean velocity by v, and weight of plane supported by their impinging action n, the number of impacts in a second or unit of time required to support the plane is $\frac{gn}{2v} = \mathrm{A}$, or $n = \frac{2}{g}\mathrm{A}v$, and this equation must evidently be maintained in altering the value of the terms. Now, it has been shown that in changing v to mv in a medium that does not alter its density we cause A to become $m\mathrm{A}$, and $\frac{2}{g}\mathrm{A}v$ becomes $\frac{2}{g}\mathrm{A}mvm = \frac{2}{g}\mathrm{A}vm^2 = nm^2$. Hence n, the weight of the plane, or measure of tension, must be increased m^2 times so that it may continue to equilibrate the impinging action. Thus, we deduce that while the molecular velocity increases from v to mv, the elasticity increases from n to m^2n or *the elasticity of a medium having a constant density is proportional to the mean square molecular velocity or* vis viva *of the medium* (or $e \doteqdot v^2$, when Δ^3 is constant)* . . . . . III.

* [II. and III. were given by D. BERNOULLI. See 'POGG. Ann.,' vol. 107, p. 490, 1859.—R.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

§ 5. Combining II. with III. it appears that when both the density and the *vis viva* are subject to change that the elasticity is equal to their product, or $e \doteqdot \Delta^3 v^2$, and this is the law that includes all the conditions of equilibrium of an enclosed homogeneous medium. One other condition only remains to be specified. *Under a constant pressure the density is inversely as the* vis viva *or mean square molecular velocity* ($\Delta^3 \doteqdot \frac{1}{v^2}$, if e is constant) . . . . . IV.

§ 6. In concluding this part of the subject, we cannot fail of being sensible of the analogies that subsist between these synthetical deductions and the chief properties that distinguish aeriform fluids.

The first point that was inductively established is MARIOTTE'S law, viz.: *at the same temperature the density of air is as its compression.* This is analogous to the second deduction:—The square of the velocity being constant, the elastic force of a medium is proportional to its density. The accordance appears as complete as could be desired, and there is a residual evidence in favour of v^2 being identical with temperature, or being a quality that varies simultaneously with it.

The second point is DALTON and GAY-LUSSAC'S law of expansion. By experimenting upon the same weight of air at different temperatures under a constant pressure, these philosophers found that an increment of one degree caused always the same augmentation of bulk, and that this amounted to $\frac{1}{480}$th part of the space that it occupied at 32°. Thus, if the same law hold good at all temperatures, 480 cubic inches of air at this temperature should diminish one inch in bulk for every degree it was lowered in temperature, and would become zero in bulk at 480° below the freezing point of water, or − 448° on Fahrenheit scale.

Now in IV. we had $\Delta^3 \doteqdot \frac{1}{v^2}$, or $v^2 \doteqdot \frac{1}{\Delta^3}$, when e is constant; but $\frac{1}{\Delta^3}$ is the volume occupied by a constant number of molecules; hence with the same constant number of molecules the volume is as the mean square molecular velocity, and a constant increment of *vis viva* is followed by the same increment of volume under a constant pressure, and as the constant increment of volume (1 cubic inch) is to the constant increment of *vis viva* (1°) so is the volume (480 cubic inches) corresponding to a certain *vis viva* (32° Fahr.) to that *vis viva* (480°).

The analogy therefore still holds good, and the evidence continues in favour of the absolute temperature being represented by v^2.

When air is not allowed to expand and heat is applied, the elastic force increases with the temperature, and a rise of 1° causes an absolute increase in the elasticity, which is the same at all temperatures, and corresponds with the increase of bulk it would assume if allowed freely to expand. This is analogous to III., where, the density being constant or bulk unchanged, the elasticity is shown to be proportional to the mean square molecular velocity.

Thus, the laws of MARIOTTE and of DALTON and GAY-LUSSAC are represented by

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

the formula $(448 + t)\,\Delta^3 = e$; in which $t =$ temperature, Fahrenheit scale; $\Delta^3 =$ density, and $e =$ elasticity.

The law of elasticity in the hypothetical medium is represented by the formula $v^2\Delta^3 = e$; in which v^2 is the mean square molecular velocity; $\Delta^3 =$ density, and $e =$ elasticity.

The *first* expresses physical laws that have been *found* to belong to a certain *existent* form of matter.

The *second* expresses physical laws that have been *proved* to belong to a certain *possible* form of matter.

The cause of the effect represented by $(448 + t)$ in the first is unknown, but has, at various times, by eminent authorities, been referred to *molecular motion.*

The corresponding term, v^2, of the second represents *molecular motion.*

Section II.—On the Physical Relations of Media that differ from each other in the Specific Weight of their Molecules.

§ 7. The synthetical deductions of last section apply to a homogeneous medium without respect to the absolute weight of its molecules, if the weight of each molecule is the same. This weight, common to all, may be viewed as the specific molecular weight of the medium, and distinguishes it from any other medium with a different specific molecular weight. We have now to enquire into the relations that subsist between the density and molecular velocity of two such media that have the same elasticity, or that are in equilibrium of pressure and also of *vis viva.*

We deduced from the law of impinging elastic bodies that if v represents the mean molecular velocity in feet per second, A the number of molecular impacts in a second upon a small elastic plane which is equal in weight to n molecules, then $n = \frac{2}{g}\mathrm{A}v$. Let ω represent the specific weight of the molecules, we have $\omega n = \frac{2\omega}{g}\mathrm{A}v = e =$ the elastic force exerted by the medium on a unit of surface;* and as this must in the present enquiry be assumed constant, we may easily remark how a change in ω affects v and A.

It is evident that since $\frac{2\omega}{g}\mathrm{A}v$ is a constant quantity and ω, A, and v variable, we have $\mathrm{A}v \doteqdot \frac{1}{\omega}$; but $e = \omega\Delta^3 v^2\,(\S\,5) = \frac{2\omega}{g}\mathrm{A}v$, and, therefore, $\Delta^3 v = \frac{2}{g}\mathrm{A}$, or $\mathrm{A} = \frac{g}{2}\Delta^3 v$, and $\mathrm{A}v \doteqdot \frac{1}{\omega} \doteqdot \Delta^3 v^2$. Hence it is obvious that if Δ^3, the density or number of molecules in a constant volume, as well as e, the tension, are constant, while the molecular

* e is the absolute weight of the small elastic plane that is supported by the succession of A number of molecular impacts per second, the weight of each of which is ω, and their common impinging velocity v feet per second.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

velocity and specific weight are variable, these variables are bound by the relation expressed by $v^2 \doteqdot 1/\omega$, which signifies that if two media are in equilibrium of pressure and have in the same volume of each the same number of molecules, the squares of their molecular velocities must be inversely as their specific molecular weights. Hence, we deduce that *if any number of separate media have equal density and tension, the molecular velocity of each must be proportional to the inverse square root of their specific molecular weight, or to the inverse square root of the specific gravity of the media respectively* * . . . . . V.

§ 8. But media may be in equilibrium of pressure without being of equal density, for a deficiency of density may be compensated by an excess in the molecular velocity. It is plain that if e and v^2 are constant in any two media they may still be in equilibrium of pressure if ω is proportional to $1/\Delta^3$, or if the molecular weight of each medium is inversely as its density. If the specific molecular weights are in a constant ratio to each other and the tension and velocity also constant, the media must be kept in equilibrium of pressure if the density of each is reciprocally proportional to the specific molecular weight of the other.

We have supposed hitherto that the media are separate while their respective elasticities are compared. Let us now enquire into the effects of allowing them to have access to each other. The united media immediately obtain a heterogeneous character, for it requires no demonstration to convince us that the molecules of each will permeate through the volume occupied by the other, the vacuities in the space occupied by each presenting no more obstacle to the motion of one set of molecules than it does to the other; and as collision must take place amongst them in every possible manner and direction, the common space of the united media are free alike to each individual molecule of both to range through in its zig-zag course. Consequently, *media in contact with each other become gradually equally diffused through their common volume* . . . . . VI.

The internal condition of the mixture must after a time become settled so that in any infinitesimal portion the same mean velocity will be found proper to the molecules of each medium respectively.

But as each of the two sets of molecules, although completely mixed together, preserve their specific weights, so must they have corresponding specific velocities that remain intact, notwithstanding that they as often impinge on molecules of the other set as on the molecules of their own kind. It is of consequence to settle what the ratio of these specific velocities is, for upon this point depends the nature of the *vis viva* equilibrium of different media, and we have to determine the relative condition of two media when they are in equilibrium both of pressure and of *vis viva*.

* [The deduction of V. appears to be correct, though much embarrassed by the irrelevant g. In his first memoir on the Theory of Gases ('Pogg. Ann.,' vol. 100, 1857), Clausius arrives at the same conclusion. His assumption that the density (in Waterston's sense) of various gases is the same, appears to have been made upon chemical grounds.—R.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

§ 9. We must now refer back to the equations of impact (§ 2). It is apparent that the sum of the impinging *vis viva* of both molecules does not alter in either the meeting or overtaking impact; what is gained by one is lost by the other, or $\beta^2B + \delta^2D = \beta_0^2B + \delta_0^2D = \beta_1^2B + \delta_1^2D$. But in every case except one a transference of *vis viva* must take place from the one to the other.

The exception is found in the meeting impact when $\beta \doteqdot 1/B$ and $\delta \doteqdot 1/D$; then shall $\beta_0 = \beta$ and $\delta_0 = \delta$, but at the same time β_1 is not equal to β, or δ_1 to δ; in every other case β_0 is not equal to β nor to β_1, nor is δ_0 equal to δ or to δ_1.

It can seldom happen that the molecules strike each other directly. In taking account of the collective result of their fortuitous concourse we must view the position of the plane of concurrence and the respective inclinations of the line of motion of each molecule to it as three independent variables. The incident velocity of each is the absolute velocity resolved perpendicular to the plane, and the equations apply to this portion only of the *vis viva* of the molecules.

Although the variety in the mode of impact is infinite, it is certain that one direction of motion is as likely as any other, and hence, that the opposite of any direction is equally probable to the direction itself.

Let us confine our attention to any single case of impact and suppose that the directions of the motions of the two impinging molecules lie on one side of the plane of concurrence, then it appears that the nature of the impact must be *overtaking*. Again, let us suppose that they lie similarly disposed on the other side of the plane; the nature of the impact is again *overtaking*. Now, instead of having the opposite of both the original lines of motion, suppose the opposite of one only is taken; it is clear that the nature of the impact is in this case of the *meeting* kind; and the opposite of the other line of motion being taken while the first is in its original position, the impact is again of the meeting kind.

Each of these four cases are equally probable, and the resolved velocities, or the values of β and δ, are the same in all, but two are meeting impacts and two are overtaking, each couple having perfectly distinct numerical equations to define the relation between the incident and reflected *vis viva*.

We are thus obliged to infer that the intestine action of the medium must be viewed in this manner as divided into two kinds of impacts specifically distinct in the numerical relation that subsists between the velocity before and after concurrence, and when employing the equations for summing up the results of the whole indefinitely great multitude that take place in mixed media, the effect of any one *meeting* impact must be considered along with its counterpart overtaking impact with the same velocities.

§ 10. We have remarked that it is only the resolved portion of the whole *vis viva* of a molecule that is dealt with by the equations—that forms the force of impact—and it may be questioned whether the mean of these forces in each kind of molecules bears the same proportion to each other as the whole *vis viva* of each. That the ratio

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

is the same is best seen by the *reductio ad absurdum* method of reasoning. If the ratio is different, the motions of the heavier molecules must be resolved in a different way from those of the lighter, or the plane of concurrence must incline to one set of molecules in a different manner to that of the other set. Now any such effect is quite inconsistent with the fundamental hypothesis, and would require us to admit the influence of a modifying power whose nature and mode of bringing about the effect in question is unknown.

The ratio ρ of the resolved to the absolute *vis viva* is actually one-third, and will become obvious in the next section, but it seems needless to require the demonstration in this place as all that we have to be assured of is the constancy of the ratio, whatever its actual value may be.

In seeking to demonstrate the nature of the *vis viva* equilibrium, the solitary condition that we have to reason from is that the mean value of $(\beta_0^2 + \beta_1^2)$ is equal to $2\beta^2$ (§ 2) and the mean value of $(\delta_0^2 + \delta_1^2) = 2\delta^2$. That this is a necessary condition is obvious, because if either were less there would be a continual transfer from the molecules B to the molecules D, or from D to B and *vice versâ*.

By squaring the equations in § 2 and adding, we have the following :—

$$\beta_0^2 + \beta_1^2 = 2\{\beta^2 - \frac{4D}{B + D} \cdot \beta^2 + \frac{4D^2}{(B + D)^2} \cdot (\delta^2 + \beta^2)\}$$

$$\delta_0^2 + \delta_1^3 = 2\{\delta^2 - \frac{4D}{B + D} \cdot \delta^2 + \frac{4B^2}{(B + D)^2} \cdot (\delta^2 + \beta^2)\}.$$

If in any case it happens that $\beta_0^2 + \beta_1^2 = \beta^2$, we shall have

$$\beta^2\left(\frac{4D}{B + D}\right) = \frac{4D^2}{(B + D)^2} \cdot (\delta^2 + \beta^2),$$

or $\beta^2 B = \delta^2 D$, and $\delta_0^2 + \delta_1^2 = 2\delta^2$. Hence, if the squares of the impinging velocities happen to be in the inverse ratio of the molecular weights, then in either molecule the sum of the *vis viva* of the twofold encounter (one *meeting*, the other *overtaking* with the same impinging velocities) before impact, or $2\beta^2$, is equal to the sum after impact, or to $\beta_0^2 + \beta_1^2$.

But this is only one case out of an infinite number where the ratio is different. Generally, we may express the equation thus :

$$\beta_0^2 + \beta_1^2 = 2\beta^2 + p, \text{ and } \delta_0^2 + \delta_1^2 = 2\delta^2 + q.$$

Now, suppose that in an indefinitely great multitude of impacts the sum of all the individual values of $\beta_0^2 + \beta_1^2$ and $\delta_0^2 + \delta_1^2$ are taken, we shall have the mean of the values of the first equal to $\beta_m^2\rho$, in accordance with the necessary condition of permanence noticed above (by β_m^2 we mean to denote the mean molecular *vis viva* or

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

mean square velocity of the B molecules, &c.). The mean value of $\beta^2 + p$ is, therefore, $\beta_m{}^2\rho$, but the mean value of β^2 is also evidently equal to $\beta_m{}^2\rho$, as above; hence, the mean value of p is 0, or the positive values of p balance the negative values. In the same way, it may be shown that the mean of the values of q is also 0. Hence, we deduce that $\beta_m{}^2\mathrm{B} = \delta_m{}^2\mathrm{D}$, or that *in mixed media the mean square molecular velocity is inversely proportional to the specific weight of the molecules* * . . . VII.

This is the law of the equilibrium of *vis viva.*

§ 11. Thus, it appears that the inverse ratio of the specific molecular weight is that which is naturally assumed by the mean square molecular velocity of media in contact, and according to the foregoing reasoning (§ 10), this is also the ratio that ensures an equilibrium of pressure between media of the same density, or which have the same number of molecules contained in the same volume. Thus, by combining V. with VII. we deduce that *media in equilibrium of pressure and* vis viva *are of equal density, or have specific gravities respectively proportional to their specific molecular weights* . . . . . VIII.

§ 12. We may likewise remark that as the mean value of the product $\beta^2\mathrm{B}$ is equal to the mean $\delta^2\mathrm{D}$, or $\mathrm{B}_m{}^2 = \delta_m{}^2\mathrm{D}$, *there is the same amount of* vis viva *or mechanical force contained in equal volumes of all media that are in equilibrium of pressure and* vis viva . . . . . IX.

§ 13. If different media are placed in contact they must diffuse themselves through their common volume with velocities proportional to their mean molecular velocity; but this velocity being in each inversely as the square root of its specific molecular weight, which is equal to the square root of its specific gravity, we may deduce, by combining VI. with VII., that *media in equilibrium of pressure and* vis viva *diffuse themselves through their common volume with velocities inversely proportional to the square root of their specific gravity* . . . . . X.

§ 14. Such are the principal points by which different media are related to each other. Their analogies to the properties of gases may be stated as follows:

(1.) The specific gravities of gases of the same *temperature* and pressure are respectively proportional to their atomic weight. [The combining equivalents or proportions may be viewed as simple multiples or divisors of the atomic weight or specific gravity.]

This is analogous to the VIII. deduction. Media in equilibrium of *vis viva* and pressure have specific gravities proportional to their molecular weight. It will be remarked that here again we have temperature represented by *vis viva.*

(2.) It is considered as almost proved that gases in equilibrium of pressure and temperature have, in equal volumes, the same absolute quantity of heat.

* [This is the first statement of a very important theorem. (See also 'Brit. Assoc. Rep.,' 1851). The demonstration, however, of § 10 can hardly be defended. It bears some resemblance to an argument indicated and exposed by Professor TAIT ('Edinburgh Trans.,' vol. 33, p. 79, 1886). There is reason to think that this law is intimately connected with the Maxwellian distribution of velocities, of which WATERSTON had no knowledge.—R.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

We have deduced, in reference to media, that when they are in equilibrium of pressure and *vis viva* they have, in equal volumes, the same amount of *vis viva*.

(3.) It is considered probable that the quantity of heat contained in equal volumes of all gases in equilibrium of pressure and temperature is proportional to their absolute temperature; and, in general, that equal increments of heat cause equal increments of temperature or expansion.

In all media in equilibrium of pressure and *vis viva* the same increment of *vis viva* causes the same expansive effect. (See also § 6.)

(4.) Gases, however different in specific gravity, when placed in connection diffuse themselves equally through each other; and according to the elegant induction of Dr. GRAHAM ('Edin. Trans.,' 1831) the velocity of diffusion is inversely as the square root of their specific gravity.

This is very exactly responded to by the hypothesis. DALTON'S law of diffusion belongs to media as a necessary and the most obvious consequence of the constitution assigned to them (VI.) DR. GRAHAM'S law of diffusive velocity or volume applies also to media, because if placed in similar circumstances such an effect must depend on the molecular velocity, which, singularly enough, bears exactly the like ratio to their specific gravity (X.).

§ 15. In the first point of analogy it was stated the atomic weight of a gas corresponded with its specific gravity, but with the reservation that the combining proportions are simple multiples or quotients of the same. This appears to me to be the fair statement of the remarkable connection that is always found between the combining volume and combining weight. It seems impossible that the fact of a volume of every gas containing the same number of molecules can ever be inductively established, but all analogy leads us to this conclusion. One volume of oxygen combines with two volumes of hydrogen to form two volumes of aqueous vapour. If we inferred from this that one molecule of oxygen combined with two molecules of hydrogen to form one of steam, we must admit that the molecule of steam occupies double the volume of a molecule of hydrogen or oxygen. If it is admitted, on the other hand, that the oxygen molecule is capable of disintegration, and that half a molecule combines with one of hydrogen to form one of steam, the bulk of the three molecules are equal. This last is the view that is responded to by the hypothetical media. The objection to it is plausible from the natural repugnance to the idea of dividing what has been considered as an ultimate element into parts, and of supposing it possible that an element should have a strong affinity to itself—for this point is also involved. Half molecules of oxygen must have a powerful attraction to each other as they never appear separate. It is the same with all the other simple gases and vapours that combine in half or other fractional volumes. We have an analogous example among the hydrocarburets. Methyl is half a molecule of olefiant gas, and enters into distinct combinations similar in every respect to those of olefiant gas, but it never appears in a separate form. Olefiant gas enters into combination with itself in

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

various proportions, forming etherine, ceten, elaen, &c., all of which are isomeric but have different specific gravities as vapours. These the chemist is unable to form directly; they are organic products and show a great molecular capability that is undoubtedly common to all bodies.

There has certainly as yet been no recognised example of a simple element appearing in the gaseous form with two specific gravities, but it would be rash to affirm that such was either impossible or absurd. Indeed, chlorine, bromine, iodine, and fluorine are so similar in their chemical qualities that it is not very unlikely they may be examples of isomeric combinations of one base in which condensation of atomic volume takes place simultaneously with increment of atomic mass. In the hydrocarburets, on the other hand, there is little, if any, condensation of atomic volume, their specific gravity in the liquid form being all nearly the same.

A strong argument in favour of the physical origin of the law of volumes is to be obtained from the combination of acids with ether. Some of these rise up into vapour in the same state of chemical union as when liquid, while others quite similar are decomposed in the act of rising and occupy double the volume of the others. Even those that are fully combined when they first rise, by an increase of temperature not very considerable, are decomposed and immediately assume a double volume. Oxalic and nitrous ethers are examples of the last kind. Sulphate and nitrate of pyroxilic ether are examples of disunion in the act of rising.

If the hypothetical law of volumes is true in all cases, we should have to distinguish between atomic weight and combining proportion. Thus, if the atomic weight of oxygen is 1 (or specific gravity of gas), its combining proportions are $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, $3\frac{1}{2}$ (?). If the atomic weight of hydrogen is 1, its ascertained combining proportions are $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, 3, 4, 5, 6, 8, 9, 16. If the atomic weight of nitrogen is 1, its combining proportions are $\frac{1}{2}$ and 1. The same for chlorine is $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$; for bromine they are $\frac{1}{2}$, 1, $1\frac{1}{2}$; for iodine, $\frac{1}{2}$, 1, $1\frac{1}{2}$; for arsenic, $\frac{1}{4}$, 1; for sulphur, $\frac{1}{6}$, $\frac{1}{3}$; for phosphorus, $\frac{1}{4}$, &c. These are necessarily derived from the specific gravity of the simple gases and of their compounds.

The labours of DUMAS, MITSCHERLICH, REGNAULT, and BINEAU, have extended the list of gases and vapours, whose specific gravities have been accurately measured, to nearly 150. Such determinations throw a light upon the atomic constitution of compounds which it is impossible to obtain from their mere chemical analysis, and form an important guide to theoretical discussion, when the arithmetic of volumes is properly applied.

SECTION III.—ON THE PHENOMENA THAT ATTEND THE CONDENSING AND DILATING OF MEDIA, AND THE MECHANICAL VALUE OF THEIR MOLECULAR VIS VIVA.

§ 16. In the first section a distinct idea of the elastic force of the medium was obtained by viewing it as a rapid succession of impacts on the lower surface of a

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

gravitating elastic plane; and the equilibrium as being maintained when the upward velocity given to the plane by the shock of one molecule was equal to the downward velocity given to it by gravity acting through half the infinitesimal portion of time that elapses between two successive impacts. During the first half of this time gravity acts in destroying the upward velocity: during the second half it acts and generates the same velocity downwards, and by applying the equation for the meeting impact (§ 2) we found the relation between the pressure and the number of impacts in a given time. This relation is expressed by $gn/2w = \mathrm{A}$, in which n is the number of molecules whose aggregate weight is the weight of the plane supported by A number of molecular impacts in a second of time: the impinging velocity being w, and g the accelerating force of gravity. It was also shown that the upward velocity given to the plane by one impact is w/n, and this is likewise the descending velocity with which it encounters the molecular shock.

We have now to examine the case where the encounter takes place with the plane at rest. Applying the equation for the meeting impact as in § 2, and putting $\epsilon = \beta = 0$; $n = \mathrm{B}$; $\mathrm{D} = 1$; $w = \delta$; we have

$$\epsilon_0 = \beta_0 = \frac{2w}{n+1} = \text{velocity upwards of the plane after the shock;}$$

$$w_0 = \delta_0 = w - \frac{2wn}{n+1} = -w + \frac{2wn}{n+1} = w - \frac{w}{n+1}$$
$$= \text{velocity downwards of the molecules after the shock.*}$$

Thus, n being an indefinitely great number, we have the ascending velocity of the plane $\epsilon_0 = 2w/n$, being double what it was in the former case when the result of the impacts was statical equilibrium: and the decrement of molecular velocity $= w - w_0 = w/n$, which is a new and important feature. In the former case there was no decrement of molecular velocity: the molecule and plane continually meeting and retreating with velocity of impact and reflexion the same, and inversely proportional to their respective weight.

With its velocity $\frac{2w}{n}$ the gravitating plane ascends to the height $\left(\frac{2w}{gn}\right)^2 \frac{1}{2}g = \frac{2w^2}{gn^2}$, so that the weight of n molecules is raised through this height by the decrement w/n of the impinging velocity w of one molecule. Employing the differential notation,

* [It is easy to see that in the case supposed $n\epsilon_0 = 2w$, when n is great, so that the velocity of the plane is $2w/n$; but in the next step there is an unfortunate error which runs through many of the subsequent deductions.

$$w_0 = \delta_0 = w - \frac{2wn}{n+1} = -\left(-w + \frac{2wn}{n+1}\right) = -\left(w - \frac{2w}{n+1}\right),$$

not $-\left(w - \frac{w}{n+1}\right)$. The *vis viva* expended in raising n to the height $2w^2/gn^2$ is thus $4w^2/n$, not $2w^2/n$.—R.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

$dw = w/n$; and $2dw\ w = 2w^2/n = dw^2$, the *vis viva* expended in raising n to the height $2w^2/gn^2$.

§ 17. If we recur to § 4 we may remark the necessity of considering molecular velocity in two points of view when applying the arguments of §§ 2 and 16 to an enclosed volume of a medium. The first point is that upon the molecular velocity of impact depends the intensity of the shock on the plane, the ascending velocity given to it, and therefore also the time between the impacts, if the weight of the plane is considered constant. Thus as any one velocity is to the time of ascent and descent of the plane caused by that velocity, so is the mean of the impinging velocities to the mean of the time intervals, or inversely as the number of impacts in a unit of time; and the equilibrium does not require that the succession of impacts should be regular; the rapidity of the succession may fluctuate, but the average time and velocity must be constant. The second point is that any augmentation of velocity causes an increase in the frequency of the encounters (§ 4). In the equation $ng/2w = \mathrm{A}$, if A were not a function of w it would remain unchanged, if n and w increased or diminished in the same proportion; but it was shown in § 4 that it was proportional to w, when Δ^3, the density, is constant, and to Δ^3 or n or c when w is constant; hence $\mathrm{A} = wc\,\Delta^3$, in which c is a constant factor that has to be determined. We have also to determine the ratio between w^2, the mean square impinging velocity, and v^2, the mean square absolute molecular velocity, in the equation $ng/2w = \mathrm{A} = wc\,\Delta^3$, or $n = \frac{2}{g}\,wc\,\Delta^3$.

Suppose the unit of volume in which the medium is confined to be a cube, the upper side of which is the plane n, and let v^2 be the mean square velocity of the molecules, so that if the squares of the respective velocities of all the molecules be added together, the sum will at all times be equal to $\Delta^3\,v^2$. Resolve the motion of each molecule at any instant into the six rectangular directions parallel to the side of the cube and add up the squares of the resolved velocities that are perpendicular to one side; it is evident that the sum must be $\frac{1}{6}\,\Delta^3\,v^2$, as the force is equally distributed in every direction, and in the stratum of the medium next the plane n one-sixth of the force of the molecules that happen to be in the stratum at any given instant is directed perpendicularly upon the plane. Suppose the breadth of the stratum is $1/\Delta$, the number of molecules that at all times are to be found moving in it is Δ^2, and half of these are diminishing their distance from the plane, and half increasing their distance with the mean square velocity $\frac{1}{3}\,v^2$.

The molecules moving equally in every direction must necessarily impinge equally in every possible direction on the plane, so that if their lines of motion were brought from every point of the surface of the plane where they impinge and made to issue from one central point, they would radiate equally to every part of the hemisphere; and as soon as those belonging to any one direction have impinged and thus withdrawn from forming part of the constant aggregate force $\frac{1}{6}v^2\,\Delta^2$, their place is

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

immediately supplied by others of the same entering the stratum. The time taken by the set whose velocity is u and inclination to the plane θ to traverse the breadth of the stratum is evidently as $\frac{1}{u \sin \theta}$, and in a unit of time the number of the impacts in the succession of these belonging to the set is proportional to $u \sin \theta$. But this is the value of the resolved velocity of the set. Referring back to the reasoning in §§ 2, 16, the supporting effect of each impact on the heavy plane n was shown to be proportional also to the velocity of impact or molecular velocity resolved perpendicular to the plane. The supporting effect of each set in a unit of time is therefore as the square of the resolved or impinging velocity of the set. But the mean of all the square impinging velocities is $\frac{1}{3}v^2$, and half the molecules in the stratum are continually approaching the plane; the supporting effect of their continuous action is therefore the same as would be derived from the medium reduced to half density advancing against the plane with the uniform velocity $\sqrt{\frac{1}{3}v^2}$. Now as Δ^3 represents the number of molecules in the cubical unit of volume, the side of the cube being the unit of length, and $\sqrt{\frac{1}{3}v^2}$ the number of such units traversed in a unit of time, the supporting effect of the medium on the heavy plane n in the unit of time, is the same as that derived from $\frac{1}{2}\Delta^3\sqrt{\frac{1}{3}v^2}$ molecules impinging with the velocity $\sqrt{\frac{1}{3}v^2}$. Hence it is obvious that $A = \frac{1}{2}\Delta^3\sqrt{\frac{1}{3}v^2}$, and $w = \sqrt{\frac{1}{3}v^2}$, or $c = \frac{1}{2}$, and $3w^2 = v^2$. Also $n = \frac{2}{g} w^2 c\, \Delta^3 = \frac{v^2 \Delta^3}{3g}$; or $v^2 \Delta^3 = 3gn$; or $v = \sqrt{3g \frac{n}{\Delta^3}}$.

Thus we obtain an expression for the square root of the mean square molecul velocity in terms of the height of a uniform atmosphere $\frac{n}{\Delta^3}$, or what is the same, in terms of the ratio of the number of molecules in a column of the medium of the height of a uniform atmosphere to the number in the column of a unit height: and since $\sqrt{2gh}$ expresses the velocity acquired by a body in falling through the height h, we arrive at the following deduction. *The mean square molecular velocity of a medium is equal to the square of the velocity that a body acquires in falling through one-and-a-half times the height of a uniform atmosphere;* if the pressure of the medium is estimated from the effects of the molecular impacts on a perfectly rigid and elastic surface. If it were estimated by the effect on molecular elastic surfaces, there is reason to believe that the mean square velocity is double the amount specified (see Sec. 4) . . . . . XI.*

§ 18. Suppose that the cubical volume of the medium receives such an increment of *vis viva* that under the constant pressure n the volume from 1 becomes $1 + \frac{2w^2}{gn^2}$; it has been shown in § 5 that the molecular *vis viva* must also from 1 have become

* [The author here arrives at the correct conclusion,

$$v^2 = 2g \cdot \tfrac{3}{2}h. \text{ —R.}]$$

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

$1 + \frac{2w^2}{gn^2}$ that it may sustain the same pressure with the reduced density. But the molecular *vis viva* in the cubical volume is $\Delta^3 v^2$: hence we have the proportion

$$1 : 1 + \frac{2w^2}{gn^2} :: \Delta^3 v^2 : \Delta^3 v^2 \left(1 + \frac{2w^2}{gn^2}\right);$$

the increment of *vis viva* in the contained medium is thus $\Delta^3 v^2 \frac{2w^2}{gn^2}$. But it has been shown in § 17 that $w^2 = \frac{1}{3}v^2$, and $gn = \frac{1}{3}v^2 \Delta^3$, hence $\Delta^3 v^2 \frac{2w^2}{gn^2} = \frac{2v^2}{n}$.

Now in § 16 it was shown that to raise the weight of n molecules to the height $2w^2/gn^2$ the *vis viva* expended was $2w^2/n = \frac{2}{3} v^2/n$; comparing this, the *vis viva* expended in the act of increasing the volume, with $2v^2/n$, the increment of *vis viva* required to support the increased volume, it is evident that the ratio is exactly one-third. Thus we deduce that *to effect one increment of expansion in the volume of a medium subsisting under a constant pressure, four-thirds of an increment of vis viva are required: one of which thirds is expended in the act and does not appear in the medium: the remaining three-thirds, or one increment, appears in the medium and assists in sustaining its augmented volume** . . . . . XII.

§ 19. This result is a necessary consequence of the perfect conservation of *vis viva* in the impinging action of perfectly elastic bodies. To enlarge a volume that is pressed upon is to raise a weight; is to expend mechanical force; is to expend molecular *vis viva*, and the last train of reasoning has led us to the relation between the molecular force expended and the work performed by it.

The mechanical value of the whole of the *vis viva* of the medium may be ascertained by the following proportion

$$\frac{2v^2}{3n} : \frac{2v^2}{3n^2} :: \Delta^3 v^2 : \frac{\Delta^3 v^2}{gn}. \quad \text{But } gn = \tfrac{1}{3}\Delta^3 v^2, \text{ therefore } \frac{\Delta^3 v^2}{gn} = 3.$$

Thus the *vis viva* expended in raising n, or the constant pressure, through the increment of the unit of volume, is to that increment as the whole *vis viva* of the medium is to three units of volume. Hence we deduce that if a medium is supposed to expand to four times its original volume with its original tension undiminished, it will in doing so expend as much as the whole of its original molecular force. This may be more concisely expressed by: *The molecular vis viva of a medium is equal to its tension acting through three times its volume*† . . . . . XIII.

* [The corrected version of XII. will be "To effect one increment of expansion in the volume of a medium subsisting under a constant pressure, *five*-thirds of an increment of *vis viva* are required; *two* of which thirds is expended in the act, and does not appear in the medium; the remaining three-thirds, or one increment, appears in the medium, and assists in sustaining its augmented volume."—R.]

† [This is the virial equation applicable under the supposed conditions.—R.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

§ 20. If a medium is not allowed to increase in volume while its *vis viva* is increasing, no force will of course be expended, and each increment of *vis viva* engenders a like increment of tension. Thus *if we compare the amount of vis viva required to produce an increment of molecular vis viva in the medium, in the two cases of constant pressure and constant volume; it is manifest that the ratio is* 4 *to* 3, *or* 4/3* . . . . . XIV.

§ 21. If we suppose the heavy plane n instead of being raised by the medium to descend upon it through the same differential height $2w^2/gn^2$, it is obvious that the same differential *vis viva* that was formerly abstracted is now communicated to the molecules of the unit volume. Force is exerted by the descending weight upon the medium and is transferred to its molecules.† Thus it is evident that the conversion of mechanical force into molecular *vis viva* is subject to the same law as the conversion of molecular *vis viva* into mechanical force. This law is expressed in XII. and XIV. The following is another form of annunciation which refers to an experimental method of ascertaining it if such media were actual existents. *The ratio of the increment of vis viva evolved by a small condensation of a medium to the diminution of molecular vis viva required to maintain the same condensation under a constant pressure is* $\frac{1}{3}$‡ . . . . . XV.

§ 22. If a medium is compressed or dilated and the molecular *vis viva* evolved in it or given out from it by the act of condensation and dilatation be retained, let us enquire into the ratio of the density to the pressure. The preceding reasoning has shown that the increment or decrement of *vis viva* is equal to one-third of the increment or decrement of density, or $\frac{dv^2}{v^2} = \frac{d\Delta^3}{3\Delta^3}$; hence $\frac{2dv}{v} = \frac{d\Delta}{\Delta}$, which being integrated gives $v^2 \doteqdot \Delta$. But $v^2\Delta^3 = e$, therefore $\Delta^4 \doteqdot e$, and $v^2 \doteqdot \sqrt[4]{e}$. Thus we deduce that *if a medium is compressed or dilated from a given condition of density and vis viva, the mean square molecular velocity varies as the fourth root of the tension or as the cube root of the density*§ . . . . . XVI.‖

§ 23. The tendency of media to have their *vis viva* augmented when being forced into smaller volume is very similar to the rise of temperature that appears in air when being condensed. Thus tinder may be inflamed by the sudden compression of a small quantity of air, and on charging an air gun the condenser and force pump become so hot as to be painful to touch. Again, mercury may be frozen if exposed to a jet of air escaping from a state of high compression and expanding against the

* [The ratio of specific heats, commonly called γ, should be 5 : 3, not 4 : 3.—R.]

† Note A (motion indestructible as matter).

‡ [This result also requires correction.—R.]

§ Note B (vapours).

‖ [The corrected argument is:—Since $dv^2/v^2 = \frac{2}{3}\, d\Delta^3/\Delta^3$, we get $dv/v = d\Delta/\Delta$, or $v \doteqdot \Delta$. Accordingly $v^2 \doteqdot \Delta^2 \doteqdot (\Delta^3)^{\frac{2}{3}}$. But $v^2\Delta^3 = e$; therefore, $\Delta^5 \doteqdot e$, and $v^2 \doteqdot e^{\frac{2}{5}}$. Also $e \doteqdot (\Delta^3)^{\frac{5}{3}}$, or $p \doteqdot \rho^\gamma$, where $\gamma = \frac{5}{3}$.—R.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

atmospheric pressure. Media also lose their *vis viva* if allowed to expand against pressure.

Thus by XVI., if at 60° Fahr. a vessel containing air of double density is allowed to empty itself into the atmosphere, the decrement of temperature in the air that remains ought to be − 48° by the XVI. deduction. If on the contrary its density is suddenly increased from 1 to 2, its temperature ought to rise to 196°.*

Thus the analogy between media and gases and between *vis viva* and temperature is still maintained, and the phenomena of latent heat in gases appear also in media as the transference of force during a change of volume: *out* of the medium when it expands, and exerts, or gives out, mechanical force; *into* the medium when it is compressed and acted upon, or receives mechanical force.

The phenomena of latent heat thus appear to be the conversion of mechanical force into molecular *vis viva;* the visible into the invisible, as in condensation: and molecular *vis viva* into mechanical force; the invisible into the visible, as in expansion.

It is a necessary consequence of the conservation of *vis viva* or indestructibity of force among perfectly elastic bodies.

§ 24. Several experiments have been made on the *ratio* of the increment of temperature evolved by a small condensation of a volume of air to the diminution of temperature required to produce the same condensation under a constant pressure, and found it to be $\frac{3}{8}$. Mr. IVORY ('Phil. Mag.,' 1827) has proved that this ratio is constant under every change of temperature or density so long as DALTON and GAY-LUSSAC's law is maintained, or the air thermometer is an exact measure of heat. MM. GAY-LUSSAC and WELTER have also proved this experimentally for a considerable range. Mr. IVORY has also expressed his opinion that the nascent value of this ratio will be found to be $\frac{1}{3}$, and that the cause is probably connected with the proportion that subsists between the linear and the solid increments of expansion.

The value of this ratio in all media, whatever may be their condition of density or *vis viva*, is $\frac{1}{3}$ (§ 21); and the synthetical demonstration rests on the same fundamental principle that determines the proportion of linear to solid increments of expansion.

This ratio $\frac{1}{3}$ applies only to infinitesimal changes of volume, and it slowly increases with the amount of condensation. When the medium is compressed from 1 to 1·20 the ratio becomes $\frac{3}{8}$.†

In the experiments of MM. GAY-LUSSAC and WELTER referred to in the 'Mécanique Céleste,' the condensation did not exceed $\frac{1}{40}$th part of an atmosphere. The discrepancy may be exactly ascertained by performing the same experiments as it were on the medium by computation. The absolute temperature is denoted by v^2

* Note C (temperature of condensed air).

† Note D (to find the compression that corresponds with a given ratio between latent and sensible heat.)

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

and the absolute zero corresponds to $-461°$ of Fahr. scale (taking RUDBERG's constant of expansion, see § 6). By employing the equation $e = v^2 \Delta^3$ and $\left(\frac{e_0}{e_1}\right)^{\frac{1}{4}} = \frac{v_0^2}{v_1^2}$; (XVI), it is easy, by substituting the barometric height for e, to compute the result of any given experiment as if it had been performed on the hypothetical medium. This I have done in the case of MM. CLÉMENT and DÉSORMES' experiments. Referring to the account given of them in the 'Mécanique Céleste,' the minus interior pressure of the medium would have been 3·42 millims.; the mean result is given as 3·61, the difference being only about $\frac{1}{130}$th part of an inch of mercury. If the experiment gave the nascent ratio, the minus pressure at the end would have been one-fourth of the minus pressure at the beginning, or 3·45 millims. In MM. GAY-LUSSAC and WELTER'S experiments, the difference of pressure at the end was 4·44 millims.; the nascent ratio in a medium would in a like experiment be 4·09 millims., the difference being about $\frac{1}{70}$th of an inch of mercury.

The evidence afforded by these experiments may be summed up as follows:—

The initial ratio of the increment of *vis viva* under a constant volume to the increment required to effect the same change of *vis viva* under a constant pressure in the medium is . . . . . $\frac{1}{1·33}$.

In air the same ratio of the increments of heat under the same circumstances by MM. CLÉMENT and DÉSORMES' experiments, is . . . . . $\frac{1}{1·35}$.

In air the same ratio, by MM. GAY-LUSSAC and WELTER'S experiments, is . $\frac{1}{1·37}$.

A difference in the reading of the height of the mercury in the manometer of $\frac{1}{130}$th and $\frac{1}{70}$th part of an inch would bring the respective experiments to coincide with the theory.*

§ 25. In the more recent of Mr. JOULE'S physical researches that gentleman has applied mechanical force to the compressing of air surrounded with water, to collect the heat evolved, and has found that about 800 lbs. descending through the height of one foot increases the temperature of a pound of water one degree. The same result nearly was obtained by forcing water through narrow tubes. Mechanical force was expended, and the same proportionate amount of heat was produced in the water. It is remarkable that the same mechanical value was found for the heat generated by the magneto-electric machine. Such accordance in the results, as Mr. JOULE remarks, seems strongly to favour the *vis viva* or vibratory theory of heat.

If air is similar in its constitution to a medium we may employ the deductions of this section to determine the mechanical value of any quantity of heat applied to it,

* [The fair agreement of the erroneously deduced value of γ, viz., $\frac{4}{3}$, with observation, was doubtless the reason of the author not discovering his mistake of calculation. We know that upon his principles the calculated value should be $\frac{5}{3}$, which accords much less well with the results observed for ordinary gases than does $\frac{4}{3}$. It should be borne in mind that the observed value, $\gamma = 1·405$, has not, even at the present time, been reconciled with theory, although reasons may be given for a departure from $\gamma = \frac{5}{3}$. —R.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

and assuming the specific heat of air to be 0·238 that of water,* we may ascertain the mechanical value of 1° applied to 1 lb. of water, which is equal to $\frac{1}{0\cdot238}$ degree applied to 1 lb. of air. Since 820 cubic feet of air at 60° and 30 in. tension weigh as much as one cubic foot of water, we have $\frac{820}{0\cdot238} = 3444$ cubic feet of air which, heated one degree without being allowed to change its volume, requires as much heat as one cubic foot of water to raise it one degree. The absolute temperature at 60° is 520°, and one degree added augments by $\frac{1}{521}$ part the absolute heat or molecular *vis viva* of the air. But the whole *vis viva* in 3444 cubic feet of air at the temperature 60° and pressure 30 in., is equal to the whole pressure of the atmosphere on a square foot, acting through three times 3444 feet in height, or 10,332 feet (XIII.). The pressure of a column of 30 inches of mercury on a base of 1 square foot or 144 square inches is equal to 14·722 lbs. × 144 = 2120 lbs. This weight raised through 10,332 ft., corresponds to 21,904,000 lbs. raised one foot high, and $\frac{1}{521}$ part of this, or 42,043 lbs., raised one foot high represents the absolute mechanical effect of 1° of heat applied to one cubic foot of water. Dividing this by $62\frac{1}{2}$, the number of lbs. in a cubic foot of water, we get 673 lbs. raised one foot high equal to the mechanical effect corresponding to 1° of heat applied to 1 lb. of water. This compared with Mr. JOULE's result is not unsatisfactory considering the difficulties that attend the experiments that afford the data.†‡

SECTION IV.—ON THE RESISTANCE OF MEDIA TO A MOVING SURFACE.§

26. The simplest case of resistance is that attending the motion of a rigid and perfectly elastic plane moving in the direction of its perpendicular.

Let the velocity of its motion be z, which we must at first assume to be indefinitely smaller than v, the square root of the mean square molecular velocity. Let a molecule with velocity u, impinge on the front surface of the moving plane at an angle θ; the impinging velocity is $u \sin \theta$; and applying the formula for the meeting impact (§ 2) the velocity of reflexion is $u \sin \theta + 2z$, and the square of this is $u^2 \sin^2 \theta + u \sin \theta\, 4z + 4z^2$. The increment of molecular *vis viva* received from the

* Note E (specific heat of air).

† Note F (M. CLAPEYRON's view of the motive power of heat examined).

‡ [This is an independent calculation of the mechanical equivalent of heat, quite distinct from that of MAYER.—R.]

§ [The weak point in the argument of this section appears to be the neglect of the effect of the altered velocities of the reflected molecules in disturbing the condition of those about to impinge. The results can only apply when the dimensions of the obstacle are small in comparison with the free path of the molecules.

The non-agreement of his theory with observations upon the resistance experienced by obstacles which do not comply with the above condition, unfortunately led the author to take the step in the wrong direction explained in §§ 27, 28. But it is proper to note that the author speaks with hesitation (§ 29). —R.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

plane is therefore $u \sin \theta \, 4z$. To find the increment given to the medium in a unit of time we have first to consider the number of impacts in the unit of time if the plane were at rest, and then the additional number owing to its motion. Referring back to the reasoning in § 17, it has been shown that the impinging velocity $u \sin \theta$ is repeated $u \sin \theta$ times in a unit of time; hence the increment of *vis viva* in the unit is $u^2 \sin^2 \theta \, 4z$, and as the mean of all the values of $u^2 \sin^2 \theta$ is $w^2 = \frac{1}{3}v^2$, we have—following the reasoning in § 17, and supposing the surface of the plane to be equal to the side of the cube that contains Δ^3 molecules—the increment of *vis viva given* to the medium by the front surface in a unit of time is $\frac{1}{6} \Delta^3 v^2 \, 4z$. By applying the same reasoning to the back surface of the plane the same amount of *vis viva* is found to be taken from the medium on that side.

We have now to consider the additional number of impacts due to the motion of the plane. Let us first suppose that no change of density is caused by the motion. The action of a medium on a surface at rest is the same as that of a uniform current of molecules whose mean distance is $\sqrt[3]{\frac{1}{2} \Delta^3}$ and velocity w (see § 17), and in the same manner the surface meeting this current with the velocity z, the effect is the same as if the velocity of the current were increased to $w + z$. The additional number of impacts due to the motion of the plane is therefore $\frac{1}{2} \Delta^3 z$, and the mean increment of *vis viva* to each being $4z$, the whole increment in the unit of time is $2 \Delta^3 z^2$. The same reasoning applied to the action on the back surface shows that the diminution in the number of impacts is also $\frac{1}{2} \Delta^3 z$, and the mean decrement of *vis viva* caused by each impact being also $4z$, we have the decrement of *vis viva* in a unit of time also $2 \Delta^3 z^3$. The sum of these $4 \Delta^3 z^2$ is the force required to move the plane with the velocity z. The weight n, whose pressure is equal to this force, is found as in the last equation of § 17: there we had $w^2 \Delta^3 = ng$, and in the same way here we have $4z^2 \Delta^3 = n_0 g$, or $n_0 = \frac{4}{g} z^2 \Delta^3$.

This result differs very much from the actual resistance of a body moving in air as observed by ROBINS and HUTTON. In HUTTON'S Dictionary it is mentioned that the resistance to a surface of one square foot, moving 20 feet per second, was found to be 12 ozs., and that it increased as the square of the velocity. Now if we compute the resistance by the formula $\frac{1}{g} z^2 \Delta^3 = n_0$, which is the common theory at low velocities, we shall find n_0 to be 15 ozs. nearly, when z is 20 feet per second, the weight of a cubic foot of air being represented by $\frac{1000}{820}$ oz.

Here then is a notable discrepancy; the resistance of the medium that represents air in specific gravity and tension appears to be four times greater than it ought to be.

§ 27. We have all along assumed, for the sake of simplicity and to avoid any addition to the fundamental hypothesis, that the surfaces upon which the medium acts are perfectly rigid as well as perfectly elastic, although no such surface, so far as

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

we know, exists in nature. If molecular *vis viva* is heat, the molecules of solids must be in motion as well as those of gases; and the nature of the motion must be such as to permit the equilibrium of *vis viva* to be established between them respectively. They must also be perfectly elastic; but a surface composed of them cannot be assumed as perfectly rigid.

The original hypothesis in respect to gases involves the necessity of making certain assumptions respecting the physical condition of the surfaces upon which media are supposed to act.

(1.) That they are composed of molecules in a state of vibratory motion which results from the struggle that their *vis insita* makes with the attractive and repulsive forces of aggregation.

(2.) The nature of these vibrations and forces may remain undefined, further than that the *vis insita* proper to a molecule is alternately destroyed at the extremities, and reproduced in the middle of each vibration when it and the surrounding molecules are in equilibrium of *vis viva*.

(3.) The impact of the molecules of a medium on the molecules of the solid surface is that of perfectly elastic bodies, and enables the equilibrium of *vis viva* to be established between them.

This equilibrium must be effected by a continual interchange of *vis viva*, the molecules of the solid giving to the molecules of the medium and *vice versa*.

In the case of a heavy molecular plane supported by the elasticity of the medium, as detailed in § 2 and § 16, the impacts that take place on the lower surface, establish both the molecular *vis viva* equilibrium, and also the statical equilibrium of the heavy plane.

Does this new condition of surface upon which the medium acts, make any change in the relation $ng/2v = \mathrm{A}$, that was shown to subsist between the impinging velocity of succession, and weight supported when the surface was assumed as perfectly rigid? Then, the molecules of the medium encountered at each impact the whole *vis insita* of the heavy plane and communicated directly to its centre of gravity a certain infinitesimal velocity. Now, it strikes a vibrating molecule which *afterwards* communicates a certain effect or infinitesimal velocity on the centre of gravity of the molecular plane. Let us endeavour to gain a clear idea of the numerical relation between the effect and the cause that produces it, viz., the impinging force of the free molecule of the medium.

The centre of gravity of the whole molecular plane being at rest while the centre of gravity of each of its molecules is in a state of intense vibration, it is evident that the track or orbit described by the centre of gravity of one of its molecules must be exactly imitated but on an infinitely reduced scale and in a reverse direction by the motion of the centre of gravity of the remaining molecules of the plane. The action and reaction of the molecular forces are equal. At any point of the orbit of one of the lower molecules of the plane let a free molecule of the medium impinge. If they are

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

equal in mass they will exchange impinging velocities; this interchange modifies the vibration and disturbs the harmony between the simultaneous motions of the centres of gravity above referred to; the motion of the centre of gravity of the molecule changes suddenly, not so with the centre of gravity of the remainder of the plane. If the connection between the plane and the molecules were broken at the instant of impact, it is clear that the centre of gravity of the remaining molecules of the plane must continue to move in the direction and with the velocity it had at the instant. Now as the concurrence may take place at any part of the vibration, either going or returning, it is plain that the mean motion of the centre of gravity of the remainder of the plane caused by the transference of *vis viva* from the molecule of the plane to that of the medium is zero. But the centre of gravity of the remainder of the plane reciprocates the active effect of the molecular force on the new velocity until it is destroyed at the end of the first vibration; the molecular force acting as much on the remainder of the plane as upon the molecule. The destruction of this by the mutual binding force destroys in the opposite direction the same amount of *vis insita* in the plane, or generates it in the same direction, and as we have to attend only to the effect upon the centre of gravity of the plane made by the motion transferred from the medium to the molecule of the plane, the mean effect must be equal to the mean incident *vis insita* of the molecules of the medium; in short the same as if the striking molecule cohered to the plane after impact. This is the case if the plane is at rest when struck, but a condition of statical equilibrium requires that the infinitesimal descending motion by gravity should be equal to the ascending infinitesimal motion given by the impetus of the striking molecules. The upward velocity therefore given to the plane by this impetus is only one half what it would be if the plane were at rest when struck (see § 2). Thus the expression $\frac{2v}{n+1}$ (see § 2) becomes $\frac{v}{n+1}$, and v/n becomes $v/2n$, and $gn/2v = \mathrm{A}$ becomes $gn/v = \mathrm{A}$.

These alterations make no difference in the subsequent reasoning until we come to § 17 where the equation for A is employed, and in consequence of its change of value the terminal equation $\Delta^3 v^2 = 3gn$ is changed to $\Delta^3 v^2 = 6gn$.

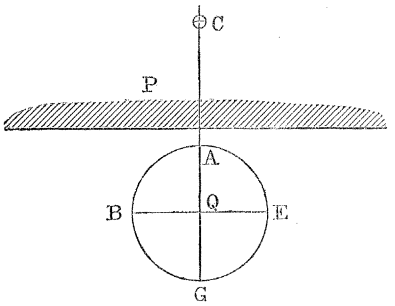
This alters the value of v from $\sqrt{3g\frac{n}{\Delta^3}}$, the velocity acquired in falling through one and a half uniform atmospheres, to $\sqrt{6g\frac{n}{\Delta^3}}$, the velocity acquired in falling through three uniform atmospheres, and the numerical value of v in the medium that corresponds with air at the temperature of melting ice is 2244 feet per second.

§ 28. As this change in the value of v reconciles the discrepancy in the theory of resistance, and in the subjects of the two concluding sections, it may be proper to illustrate by diagram the general principle that the mean impinging effect of free molecules on a cluster of cohering molecules is the same as if the striking molecules cohered at the instant of impact.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

Let P be the molecular plane consisting of $(n - 1)$ molecules, and Q one of its lower molecules at rest between attractive and repellent forces.

Fig. 1.



(1.) Let Q receive an impulse in the direction GQ, so that its initial velocity may be $QE = v$; it will proceed along the line QA until its motion is subdued at some point A by the molecular repulsive force; at the instant when the centre of gravity of the molecule Q, and centre of gravity of P, are at their minimum distance both move together with the common velocity v/n, and this is the velocity communicated to their common centre of gravity, which is not disturbed further by their mutual action during the vibratory motion that ensues. In this case there is both molecular *vis viva* communicated to Q, and also the velocity v/n to the common centre of gravity, and a free molecule of the medium has lost the velocity v.

(2.) Suppose, in the next instance, that the centre of gravity of $P + Q$ or n to be stationary, while Q is continuing its vibrations, and let it be struck when at the centre of its descending vibration by a free molecule having the same velocity QE. They will be reflected from each other without gain or loss of motion, and Q will move back towards A instead of forward to G. Here there is a loss of the down motion and the gain of an up motion. By the first (1.) the centre of gravity of P continues to ascend with the velocity $\frac{v}{n-1}$ that it has at the instant of impact; and as the downward force of Q that subdued this is gone, the centre of gravity of the whole $P + Q$ or n molecules acquires the permanent upward velocity v/n. By the second (2.) the same velocity v/n is given to the common centre of gravity by the gain of the up motion as in the first case of impact. The result of the second mode of impact is thus to communicate the velocity $2v/n$ to the common centre of gravity.

(3.) If the same kind of impact takes place with Q in the middle of the ascending vibration, it is evident that the force of impact is zero at that point, and the upward velocity to the centre of gravity zero. Now $\left(\frac{2v}{n} + 0\right) \div 2$ (impacts) $= \frac{v}{n}$. This result is more obvious if we assume the velocity of the free molecules $v + \lambda$ and that of $Q = v$. The result of the first of these is $\frac{2v + \lambda}{n}$, and of the second $\frac{\lambda}{n}$. Half the sum of these

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

is $\frac{v+\lambda}{n}$, and thus the mean result of these two equally probable impacts is the transmission of the *vis insita* of the impinging molecule to the plane as if it cohered to it after impact.

(4.) At either of the extremities of the vibration the same law obviously applies, but it is the two impacts where *vis viva* is taken from and again returned to Q whose effects ought to be viewed together. In the meeting impact let the velocity of Q from v change to u with a different direction; then according to the second case of impact the upward effect on the plane is to give it the ascending velocity $\frac{v+\overline{v-u}}{n}$, and the loss of velocity is $\overline{v-u}$. Let this loss be returned in an overtaking impact so that $\overline{v-u}$ shall become v; then according to the first case of impact the upward effect on the plane is u/n. In these two impacts Q returns to its original condition of motion, and the mean effect is v/n. A continual and equal interchange of *vis viva* being necessary to the persistent molecular condition of the plane and of the medium, the same is effected by means of impacts which take place equally in the ascending and descending vibration. This equality seems to be a necessary condition because the motions that are taken account of are the velocities of impact resolved in a vertical direction only, and the plane of impact cannot now be assumed always to be horizontal as in the case of the rigid plane; hence the absolute velocity in the vibration and the resolved impinging velocity are independent variables.

§ 29. Such is the view of the phenomena which seems to authorise the change that has been imposed on the value of the mean square molecular velocity. It has no pretension to be considered as a demonstration, and we are therefore not permitted to make use of it as a synthetical deduction from the hypothesis.

Nevertheless, if it is admitted as being probable, the probability is increased if it reconciles at once all the discrepancies that have been met with, and at the same time neither affects any one of the preceding deductions where the analogy to the properties of gases is perfect nor introduces any other point of discordance.

If we now revise the mode of estimating the law of resistance in § 26 it is obvious that the mean increment of velocity communicated by the plane now considered as molecular to the free molecules of the medium is not $2z$, but z, and hence the mean increment of *vis viva* in each incident molecule is not $4z$, but $2z$, and the increment in a unit of time not $2\Delta^3 z^2$, but $\Delta^3 z^2$. The sum of the front increment and back decrement is not $4\Delta^3 z^2$, but $2\Delta^3 z^2$; and as $w^2 \Delta^3$ is no longer equal to ng, but to $2ng$, we have $2\Delta^3 z^2 = 2ng$, or $n = \frac{1}{g}, \Delta^3 z^2$, which is the equation derived from the common theory of the resistance of the atmosphere at low velocities.

It will be remarked that the resistance is as much derived from the minus pressure behind as from the resistance in front, whereas the common theory only takes account of the inertia of the front which is assumed at low velocities as constituting the whole of the resistance.*

* Note G (objection to undulatory theory of heat).

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

SECTION V.—ON THE VERTICAL EQUILIBRIUM OF A MEDIUM, SUPPOSING IT TO FORM THE ATMOSPHERE OF A PLANET.*

§ 30. Suppose the height of the atmosphere AB to form the axis of a parabola of which the vertex A is at the summit. If a body begins to fall from A it is evident from the law of falling bodies that its acquired velocity at any point is porportional to the ordinate of the parabola at that point.

Divide AB into an infinite number of parts so that the length of each shall be proportional to the ordinate of the parabola at that part. Suppose that in each of these parts one molecule is vibrating upwards and downwards, striking against the upper and lower molecules of the adjacent parts with a velocity proportional to the ordinate of the parabola and equal therefore to what a body would acquire in falling from the vertex. It is evident that each of the parts or infinitesimal divisions will be traversed in the same time dt by its molecule, and that the impinging velocities of each pair are equal, so that there is a perfect equilibrium and constancy of phenomena; but the upper impact of a molecule against the one above it is made with less velocity than the lower impact against the one below it, because the accelerating force of gravity increases the velocity during the interval of descent, and the acceleration is represented by the increment of the parabola's ordinate in that interval. If g be the accelerating force of gravity, or velocity bestowed on a falling body every unit of time, the acceleration in each interval of descent, or infinitesimal division of the height AB, is evidently gdt. If this constant increment of velocity should by any cause be reduced in any given proportion, the aggregate effect must evidently be the same as if the force of gravity g were reduced in the same proportion.

In such a vertical column of single molecules it is apparent that the equilibrium acquires† a continually increasing velocity in the molecular motion from the summit to the base; and since the *vis viva* of a molecule is measured by the square of its velocity, it is also obvious that the molecular *vis viva* increases in the simple proportion of the distance from the summit. And knowing v^2 the amount of *vis viva* in the molecules at the base, we also know the height of the column $v^2/2g$, which is simply the height due to the molecular velocity.

§ 31. In a medium the nature of the action that sustains the upper molecules must be the same. The mean of the upper molecular impacts of a stratum must have less force

* [This section attempts to deal with one of the most difficult points in the theory. That the loss of velocity suffered by every ascending molecule will lead to a smaller mean velocity above than below seems, at first sight, inevitable. This consideration was urged by GUTHRIE ('Nature,' vol. 8, p. 67, 1873); and, in his reply (p. 85), MAXWELL narrates that a similar argument, which occurred to him in 1866, nearly upset his belief in calculation. WATERSTON'S result really depends upon an assumption that, at a given height, the molecular velocities are all the same; whereas, according to the true Maxwellian law, all velocities are to be found at all heights. The force of this consideration will be appreciated when it is remembered that those molecules which at any time move at a low level with low velocities, would not of themselves reach a high level at all.—R.]

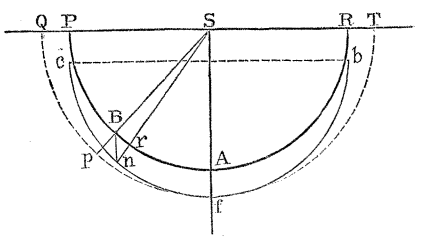
† [? requires.—R.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

than the mean of the lower, the difference being the accelerating effect of gravity in the breadth of the stratum. We have also to remember that the nature of the equilibrium of a medium requires that if the velocities of all the molecules that pass a horizontal or other plane in a given time are resolved perpendicular to that plane, the sum of the squares of these resolved velocities are equal in opposite directions. In a constant infinitesimal time the absolute acceleration of velocity is evidently greater with the vertically moving molecules than with those moving obliquely to the vertical; thus the aggregate effect of the accelerating force of gravity in increasing the molecular velocity must be less than if it acted upon them directly as in the vertical column (§ 30). The question is, how much less? for in such proportion must we consider the force of gravity to be reduced, supposing it to act uniformly on all the molecules of the atmosphere. The retardation of the ascending molecules of a stratum is equal to the acceleration of the descending molecules. Let us consider the latter.

We assume from the original hypothesis that in any infinitesimal area the lines of molecular motion lie equally in every direction, so that if supposed to issue from one point S, they would be directed equally to every point of the surface of a sphere of which S is the centre. Let SB represent one of these velocities and Bn the vertical

Fig. 2.



acceleration by gravity in the infinitesimal time dt. With the radius SB describe a hemisphere having its base on the horizontal plane PS. It is evident that the locus of the point n is the surface of another hemisphere with its base at the distance of Bn below the plane PS, and that the area of the space between the bases is equal to the area between the surfaces of the hemispheres. Now, if gravity acted on each line of molecular motion, instead of acting only in the vertical, the common increment of velocity that would affect all is $Bp = Bn = gdt$; and this, when Bn/BS is infinitesimal, is equal to the quotient of the area between the concentric hemispheres qpfT, PBAR, by the surface of the inner hemisphere. But the actual increase of BS is $nr = n\mathrm{S} - \mathrm{BS}$, and the mean increment is found by adding up all the particular values of nr, and dividing the sum by the number of values, or, what amounts to the same thing, taking the quotient of the area between the equal hemispheres PBAR, $cnfb$ by the surface of one of them. Now the first is equal to the area between the bases, which is equal to the product of a great circle by Bn, and the latter is well known to be equal to two great circles; therefore the quotient is $\frac{1}{2}Bn$.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

Thus, it seems to be clear that the molecules of a medium are collectively only half as much affected by gravity as if they all moved in vertical lines; but it has been shown (§ 30) that if they moved in vertical lines the height of the atmosphere would be the height due to the molecular velocity; but as the increments of their velocity by gravity is only one-half what they would receive if their motion were vertical, that height must be computed as if the force of gravity were only one-half the actual amount. Thus, if v^2 be the mean square velocity at a depth H below the summit of the atmosphere, the height due to this with the full effect of gravity is $v^2/2g$, and with half effect it is $v^2/g = \mathrm{H}$. Thus we arrive at the following deduction. *The molecular* vis viva *increases simply as the depth below the summit of the atmosphere, and the height of the summit above any stratum is equal to the quotient of the mean square molecular velocity at that point by the accelerating force of gravity, or to double the height that a free and unresisted projectile would ascend if projected vertically with an initial velocity equal to the square root of the mean square molecular velocity in the stratum*. . . . . XVII.

§ 32. To ascertain the law of density we have the equation in § 17, modified as in § 27 to $\frac{1}{6}\Delta^3 v^2 = gn$, for the reasons given in last section. By this we have $v^2/g = 6n/\Delta^3 = \mathrm{H}$, which applies to any part of the atmosphere at all heights.

Differentiating the equation $\frac{6n}{\Delta^3} = \mathrm{H}$, we have $\frac{6dn}{\Delta^3} - \frac{6n3d\Delta}{\Delta^4} = d\mathrm{H}$. But $\frac{dn}{\Delta^3}$ is evidently equal to $d\mathrm{H}$, and $\frac{6n3d\Delta}{\Delta^4} = \frac{6n}{\Delta^3} \times \frac{3d\Delta}{\Delta} = \mathrm{H}\,\frac{3d\Delta}{\Delta}$; therefore $\frac{6dn}{\Delta^3} - \frac{6n3d\Delta}{\Delta^4} = d\mathrm{H} = 6d\mathrm{H} - \mathrm{H}\,\frac{3d\Delta}{\Delta}$; or $\frac{3d\Delta}{\Delta} = \frac{5d\mathrm{H}}{\mathrm{H}}$; and by integration we have $\Delta^3 \doteqdot \mathrm{H}^5$. Thus we deduce that *the density of the medium at any depth below the summit of an atmosphere is proportional to the fifth power of that depth* . . . . . XVIII.

§ 33. As we had $v^2 \doteqdot \mathrm{H}$ we may further deduce that $v^2\Delta^3 = \mathrm{H}^6$, or that *the elastic force of the atmospheric medium at any point is proportional to the sixth power of the depth of that point below the summit and to the sixth power of the mean square molecular velocity* . . . . . XIX.

These deductions are all embraced by the equations $v^2/g = \mathrm{H} \doteqdot \Delta^{\frac{3}{2}}$, and $v^2\Delta^3 \doteqdot \mathrm{H}^6 \doteqdot \overline{v^2}|^6$.

§ 34. To compare these results with what is known of the physical condition of our atmosphere, we have first the obvious correspondence between the diminution of molecular *vis viva* and of temperature in ascending. No sufficient explanation of this has, I believe, been yet offered, for it is needless to attempt to do so by supposing the specific heat of air to increase as its density diminishes, as no difference of specific heat disturbs the equilibrium of the temperature of bodies placed in horizontal contact. The very fact of a gaseous atmosphere presenting a constant inequality of temperature at different elevations seems to prove that the law of the vertical equilibrium of temperature is essentially different from the law of horizontal equilibrium.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

The actual rate of diminution is very fluctuating and uncertain, varying from 200 to 500 feet for each degree. The formula of our hypothesis applies only to the condition of an atmosphere resting on a horizontal base; such, indeed, as may be found only during a balloon ascent.

M. GAY-LUSSAC, in his celebrated ascent from the neighbourhood of Paris, found the depression amount to $72\frac{1}{2}°$ Fahr. in 7634 yards. This corresponds to 316 feet of elevation to 1°, if the rate is uniform. We have already determined (§ 27) the value of v in air at the temperature of melting ice to be 2244 feet per second; hence $v^2/g = 156{,}593$ feet $=$ H, the height of the atmosphere at this temperature (being nearly 30 miles). Now, taking RUDBERG's expansion of dry air, the value of v^2 in degrees of Fahr. is 493° at this temperature, and $\frac{156593}{493} = 317{\cdot}6$, which is the elevation that ought to correspond to 1° by the hypothesis, in which also the rate is uniform. If DALTON and GAY-LUSSAC's constant of expansion is preferred, the elevation for 1° is 328 feet.

The hypothesis requires that the diminution of temperature should be uniform, and the best authorities agree that it approximates to uniformity at considerable elevations. In M. GAY-LUSSAC's table of observations taken during his ascent, the indications of the thermometer are somewhat irregular, as might be expected from the manner of making the observations, and the formula (LAPLACE's) employed to compute the elevations may not, perhaps, answer so well for balloon ascents as it has been found to do in mountainous elevations. We have also to keep in view that the atmosphere absorbs a large proportion of the Sun's rays in their passage through, besides being supplied with heat from the ground irregularly according to the varying characteristics of its surface. Taking all these circumstances into account, the accordance between theory and M. GAY-LUSSAC's extreme observations is nearer than might be expected, and probably will not be found so exact at lesser elevations.

But the hypothesis admits of being tested without employing any empirical barometric formula, because, if it is correct, the tension as shown by the column of mercury ought to vary as the sixth power of the absolute temperature (from zero at $-461°$ Fahr.) (XIX). But the observations must be taken at stationary points during the ascent, so that time may be allowed for the thermometer to acquire the temperature of the stratum of air in which the balloon rests. Let $z°$ be the absolute temperature of Fahr. zero; then for any two observations we ought to have $\left(\frac{z+t_1}{z+t_2}\right)^6 = \frac{e_1}{e_2}$; in which t_1, e_1, are the temperature and tension at any one altitude and t_2, e_2, the same at any other. The value of z eliminated from this equation ought to be 448 or 461. I have tried this with M. GAY-LUSSAC's sixteenth and last observations, which appear to be the most favourable for accuracy, and z comes out equal to 467. The rate of diminution also in the interval of 1800 metres between these two observations agrees well with theory, being 310 feet for each degree Fahr.*

* Note H (Formula for measuring heights by thermometer).

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

§ 35. We must now endeavour to show that an atmosphere of mixed media follows exactly the same law of equilibrium.

Atmospheres of different homogeneous media supposed separate from each other must evidently have the same height if the mean square molecular velocity at the base of each of them is the same, and, consequently, the molecular *vis viva* in each atmosphere will, at the same height, be proportional to the specific molecular weight of the medium. If, on the contrary, the molecular *vis viva* at the base of each is the same, then will the height which is proportional to the mean square molecular velocity follow the inverse ratio of the specific molecular weight, which is also equal to the direct ratio of the mean square molecular velocity (VII.). Thus, a hydrogen atmosphere ought to be four times the height of an oxygen atmosphere, &c. When mixed, the molecules of each of the media at the same height are necessarily in equilibrium of *vis viva*, and the mean space occupied by each molecule is therefore the same (§ VIII.). To see distinctly that the condition of the mixture is exactly that of a homogeneous medium of equal specific gravity, or, what is the same, whose specific molecular weight is equal to the sum of the products of the specific molecular weight of each by its proportionate volume—and thus having in equal volumes the same amount of *vis viva* as the mixture—we have only to recollect that a constant increment of descent in the atmosphere corresponds in all parts of it to the same constant increment of mean square molecular velocity, whatever the molecular velocity may be, or whatever the weight of the molecules with which it is associated, and the increment of *vis viva* in each medium for the same constant increment of mean square molecular velocity is as the product of its specific weight by its constituent volume. But the increment of mean square molecular velocity in the homogeneous being the same as in each of the constituents of the heterogeneous medium, and the product of its specific weight by its constituent volume being equal to the sum of the products of the specific weight and constituent volume of each, it is obvious that for the same increment of descent through the atmosphere the increment of *vis viva* in the homogeneous is the same as in the mixed medium, and that generally the physical condition of an atmosphere consisting of various media mixed together is exactly the same as if it were composed of one homogeneous medium whose specific gravity is equal to that of the mixture.

If each constituent of an atmosphere were supposed to form an atmosphere by itself, and ranged by each other side to side, and having all the same height, the ratio of their densities or proportional number of molecules in a constant volume would be the same at all heights, but the molecular *vis viva* would be respectively as the specific weight of each. If in this condition they were brought together so that all might occupy the space of one, an immediate change in the molecular *vis viva* of each medium would ensue, the heavy molecules losing and the light molecules gaining *vis viva* until the *vis viva* equilibrium is established; and this, as well as their united density, corresponds with the same qualities of the homogeneous medium at

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

the same height. All this is an obvious corollary of what precedes. *The vertical condition of equilibrium of an atmosphere is the same whether that atmosphere consists of one homogeneous medium or of a mixture of different media having the same specific gravity* . . . . . XX.

§ 36. The relation between the total height of an atmosphere of the medium to the height due to the molecular square velocity (XVII.) enables us easily to estimate the effect of diminished gravity, and assign the limits of temperature at the base, beyond which an atmosphere cannot be retained.

If the force of gravity is constant, it has been shown that the height of the atmosphere is equal to the height a body would ascend with the molecular velocity, and supposed to be acted upon by half the force of gravity; but as it really diminishes as we ascend, according to the ratio $\left(\frac{R}{R+H}\right)^2$ (in which R is the radius of the planet and H the height above its surface), the true height must be computed with the variable half-force $\frac{g}{2}\left(\frac{R}{R+H}\right)^2$, instead of with the constant half-force $\frac{g}{2}$.

Let v be the initial velocity of the vertical projectile at the surface of the planet, w its velocity at the height h; then shall $\frac{dh}{w} = dt$, and $dt\ \frac{g}{2}\left(\frac{R}{R+H}\right)^2 = -dw =$ the retardation in the differential time. Substituting the value of dt, the differential of the time in this equation, we have $-dw = \frac{dh}{w}\cdot\frac{g}{2}\cdot\left(\frac{R}{R+h}\right)^2$, and multiplying by $2w$ we have $-2w\,dw = -dw^2 = dh\,g\,.\left(\frac{R}{R+h}\right)^2$. Integrating this expression gives $v^2 - w^2 = Rg\left(1 - \frac{R}{R+h}\right)$, so that when $w^2 = 0$, we have by eliminating h (which then represents the total height of the atmosphere) $h = \frac{Rv^2}{Rg - v^2}$; being its value in terms of the radius of the planet, of the mean square molecular velocity at its surface, and of the force of gravity at its surface. In the former expression for H, where the force of gravity was supposed constant, we had $H = v^2/g$, or $v^2 = gH$. Substituting this value of v^2 in the equation for h, we have $h = \frac{H}{1 - \frac{H}{R}} = H\left(1 + \frac{H}{R}\right)$, if H^2/R is infinitesimal in respect to unity.

Thus the correction to be applied for the diminishing power of gravity in ascending increases as the square of the height, and employing the preceding data, the total height of the earth's equilibrated dry atmosphere, considered as a medium at the temperature of melting ice, is by this theory 157,776 feet, being 1183 feet more than the last determination, with constant force of gravity; and the correction to be added to the height computed with constant force of gravity is in feet $1{\cdot}2 \times H^2$, the square of the height in miles.

§ 37. We may express the last equation in a more general form with the molecular *vis viva* as the constant instead of the mean square molecular velocity. If the

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

specific weight of the medium that corresponds with air is taken as unity, and $1 \times v^2$ is the value of the molecular *vis viva* at the surface of the planet: with any other medium whose specific weight is s, its mean square molecular velocity with the same *vis viva* is v^2/s, (VII); and the absolute height of its atmosphere is $h = \frac{Rv^2}{Rgs - v^2}$. This equation gives the absolute height of an atmosphere under every variety of condition, and determines the limit of *vis viva* at the surface of a planet beyond which the medium cannot be retained, for when h is infinite we have $Rgs - v^2 = 0$ or $v^2/s = Rg$. With regard to the medium that represents the atmosphere of our planet, we have already determined the value of v^2 to be $(2244)^2$, when the absolute temperature is 493° and $s = 1$; consequently, when $v^2/s = Rg$, the surface temperature must be 65,760° Fahr. for air, and 4556° for a hydrogen atmosphere whose specific weight s is $\frac{1}{14432}$. At these surface temperatures such atmospheres would slowly evaporate into space.*

At the surface of the Moon the limit of temperature for an atmosphere of air is 3008° absolute or 2505° on Fahr. scale. For a hydrogen atmosphere it is 208° absolute or − 253° Fahr. But the proximity of the Earth reduces these limits respectively 100° and 7°, so that if the Moon's surface had even a higher temperature than 2405°, the Earth, according to this theory, would then gradually withdraw the whole of any atmosphere of air that it might then have possessed.

By employing the same equation, it appears that the temperature at the surface of a body like the Sun in magnitude and mass requires to be 13,400° to sustain an atmosphere identical in constitution and height to that of the Earth.†

§ 38. It will not fail to be remarked that the positive evidence in favour of the reasoning of this section turns on one point. Does the law of vertical equilibrium of temperature correspond with the law of vertical equilibrium of *vis viva?* We have seen that the correspondence is more exact than might be expected, although it is extremely difficult to put the question to the test of direct experiment. In a column of air 318 feet high the temperature at the bottom ought to be 1° higher than at the top in any state of the atmosphere. If air is made to circulate quickly in two tubes of this height lined with non-conducting material, the difference of temperature ought to be very distinctly shown by thermometers at the top and bottom. The quick motion of the air downwards and upwards may be expected to compensate for the disturbing effect of the sides of the tube, and even to cause their internal surface to assume the proper atmospherical gradient of temperature.

The accuracy of the formula for measuring heights by the barometer that may be derived from the deductions of this section depends on the integrity of the law of diminution of temperature, but as this varies from local causes, the theoretical rule does not seem to apply so well as those in common use, which are partly empirical.

* Note K (central heat).

† Note L (nebular hypothesis).

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

But a strictly theoretical formula may be deduced if it is permitted to assume that the change of temperature between two stations is uniform, whatever that difference may amount to, and likewise that the change of density is conformable.*

SECTION VI.—ON THE VELOCITY WITH WHICH IMPULSES ARE TRANSMITTED THROUGH A MEDIUM.†

§ 39. The reasoning on the subject of this section is founded on the principle that the velocity must correspond with the average velocity resolved through the medium in any one direction.

We have seen in § 17 that the mean square velocity resolved in one direction is equal to one-third of that mean square velocity, and it is easy to prove, if all the velocities of the molecules are equal, that the average resolved velocity in one direction is equal to one-half the common velocity.

As the equal lines representing the molecular velocities on one side of a plane may be assumed to radiate equally in every direction from one point, they will spread to every point of the hemisphere, resting on the plane; let perpendiculars be dropped from these points upon the plane. *The quotient of the sum of these divided by their number is equal to half the common length of the equal lines.* The proof of this is derived from the integration of simple circular functions that give the quotient of the sum of the sines of a hemisphere divided by their number, or by the surface of the hemisphere, equal to half the radius. Thus, if θ be the inclination of the radiating lines to the plane, $v\,d\theta \sin\theta \cos\theta\, 2\pi$ represents the aggregate of the perpendiculars upon the base of the hemisphere, and $d\theta \cos\theta\, 2\pi$ represents their aggregate number. Collecting the quotients of the first by the second for every value of θ from 0° to 90°, or what is the same, integrating these functions, and dividing the first by the second, we have the quotient equal to $\frac{1}{2}v$, which is the mean velocity resolved perpendicular to the stratum when the molecular velocity v is constant.

§ 40. But the hypothesis does not admit of the molecules having all the same

* Note M (barometric formula).

† [The idea of the direct connection between the velocity of sound and that of the molecules is of great interest, and leads at once to the conclusion that the velocity of sound is independent of density, but proportional to absolute temperature. The next person to raise the question was STEFAN ('POGG. Ann.', vol. 118, 1863, p. 494), but his calculation is as defective as that of the author. On WATERSTON'S principles, the ratio of the velocity of sound to the molecular velocity of mean square should be $\sqrt{5/3}$, as was shown by MAXWELL (PRESTON, 'Phil. Mag.,' vol. 3, 1877, p. 453). In the 'Philosophical Magazine' for 1858 (vol. 16, p. 481) WATERSTON returned to the subject. It is curious that he regarded the ordinary hydrodynamical investigation, not merely as needlessly indirect, but as inconsistent with the molecular theory. A result in harmony with experiment cannot be obtained on the basis of a hypothetical medium constituted of elastic spheres, for such a medium would have a ratio of specific heats different from that observed in gases.—R.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

velocities; we have therefore to enquire into the effects of this diversity upon the velocity of transmission.

The molecules in a small sphere of the medium at any given instant may be classed in respect to their velocity into sets, and of each set we are allowed, by the hypothesis which we are following, to assume that there is an equal number moving in every direction, and that since continuous uniformity in the density requires that the number contained in the spherical space should be always the same, the exit of one of a set may be conceived to be immediately followed by the entrance of another of the same moving in the same direction and with the same velocity. One-half the number in a set is increasing their distance from a given plane, and the other half diminishing their distance. Let the motions of one of these halves be resolved in the direction perpendicular to this plane, and let us add together such resolved spaces as are described by all the molecules of the set that happen to be in the sphere during a constant time for so long as they remain in it, and divide by the constant number of molecules of the set in the sphere at all times; the quotient must evidently be the mean velocity in that direction and set, and must be the uniform rate with which an impulse is conveyed in one direction by means of an infinite series of impacts, the space between two impacts measured in the constant direction being the step forward made by the infinitesimal portion of the impulse contained in the traversing motion of the molecule from one of the impacts to the other.

The number moving in any one direction with the velocity u is equal to the number moving in any other direction with the same velocity, and each of these numbers takes the same time to traverse the sphere. If we compare this time with that taken by the molecules of another velocity or set, it is obvious that these times must be inversely as the velocities, and *the number that continuously pass through the sphere or any other constant space in a constant time must be as the velocity:* for this may be estimated as if there were continuous currents of molecules moving in every possible direction with the respective velocities; the encounters that may be imagined to interrupt this continuity being infinite in number do not alter the general average of velocity or direction or proportionate number, and therefore each velocity and direction may be taken as constant. Now, for any one velocity u viewed thus as constant, the mean resolved velocity in one direction of all the molecules that happen to move with this velocity at any instant is, as above demonstrated, equal to $\frac{1}{2}u$; *but if we add up the resolved spaces traversed by all the molecules that have been in the sphere with this velocity during a constant time, and divide by the constant number that are in the sphere at any instant,* we require to multiply $\frac{1}{2}u$ by a factor that is proportional to u, so that $\frac{1}{2}u^2$, the resulting product, is proportional to the mean distance traversed in a constant time by the molecules that have appeared in a constant space to move with this velocity during the constant time.

Now, suppose an impulse to be given to the medium at any point, and an indefinitely long cylinder of the medium to extend from this point; the impulse

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

given to the molecules at its extremity can be conveyed through the medium only by means of the molecular encounters, each of which contributes to this effect with different velocities resolved in the direction of the cylinder. It has been shown that the mean traversed distance in a given space during a given time due to any one molecular velocity is as the square of that velocity multiplied by the proportion of the number of molecules associated with it. Therefore, the united effect of all velocities must be equal to the sum of these products, and this sum is unity, or the whole medium multiplied by the mean square molecular velocity. But it was shown that if the molecular velocity were constant and equal to v, the absolute value of the mean resolved velocity, or traversed distance, during a constant time in one direction, would be $\frac{1}{2}v$. Now, as the traversed distance or transmitting effect of this velocity in comparison to the other velocities u, &c., as they actually exist in the medium, is as v^2 to u^2, &c., we arrive at the conclusion that $\frac{1}{2}v$ is actually the uniform velocity with which an impulse is transmitted through a medium.

§ 41. According to the reasoning in §§ 27 and 28, the value of v is the velocity acquired in falling through three uniform atmospheres. This gives $\frac{1}{2}v = 1122$ feet per second at the temperature of melting ice, and 1176 at the temperature of 80°, being an increase of $\frac{2}{3}$th of a foot for each degree. In the article, "Acoustics," 'Penny Cycl.,' it is stated that 1125 feet per second at 62° accords nearly with the mean of the best experiments, and that the difference for 1° is $\frac{8}{7}$ths of a foot. The velocity by the hypothesis is therefore about $\frac{1}{40}$ part greater than is found by observation, which, in a distance of 8 miles, amounts to a difference of one second in the time of travelling that distance. This is probably a greater difference than can be allowed between observation and a correct theory. M. MOLL's observations, which seem to be standard authority, were taken with such precautions that an error of 1 in 40 seconds can hardly be admitted. They likewise agree remarkably well with Mr. GOLDINGHAM's observations at Madras.

In taking astronomical observations of the same kind with the same instrument, it has lately been discovered that two individuals differ sensibly from each other. This has led to the suspicion that in all observations there is a personal error due to some obscure physiological cause that allows a small interval of time between sensation and perception, or volition. If this were the same for the sense of hearing as for vision, it could not affect the results of experiments on sound; but it is quite possible that it may be different, and the very fact that such personal errors do exist, may justify a suspicion that such an effect might interfere and prevent a perfect degree of accuracy from being obtained.

We have made no hypothesis of the nature of the impinging surfaces of the molecules. May the discrepancy arise from something omitted in this?

In other media, according to this theory, the velocity varies as the inverse square root of their specific gravity, and at different temperatures as the square root of the absolute temperatures. It depends wholly on the thermometer, and is quite inde-

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

pendent of the indications of the barometer. This accords with the generally received theory. The molecular velocity of watery vapour being to that of air as $\sqrt{14{\cdot}4}$ to $\sqrt{9}$, the moisture in the atmosphere ought to have the effect of accelerating the velocity about 4 feet per second in temperate latitudes and 10 feet in the tropics at a maximum.

Notes.

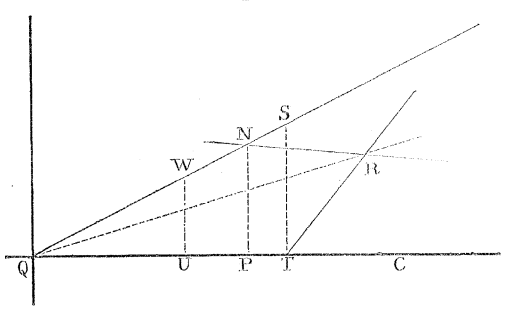
Note A.—Motion Indestructible as Matter.

The force of the descending weight is apparently *expended*, but it is only *transferred* to the medium. If the elements of matter are perfectly elastic, this kind of transference must be of general occurrence wherever force is exerted, because the exertion of force is then but its transference either from its invisible constant condition, as in the medium, to its visible transitory condition, as in the ascent of the weight, or *vice versâ*. In the former case force exists in the matter of the medium without change; in the latter it is being transferred to the agent of gravitation, so to speak, and apparently released and disconnected from matter. The force of a medium, when it equilibrates a force of gravity, is similar to the force of a wind or a current of water on a stationary surface. Is it not possible to view all forces as inseparable from some form of matter, and all the phenomena of nature, as not consisting of the creation and annihilation of force, but in its transference from one form of matter to the other?

Note B.—Vapours.

This enables us conveniently to represent the relation between the density and the square root of the mean square molecular velocity of a medium while it is being dilated or compressed.

Fig. 3.



Take Q as the origin of co-ordinates, and let QP represent v and PN the $\sqrt{\frac{1}{\Delta}}$. Join NQ. If the medium is compressed so that $\sqrt{\frac{1}{\Delta}}$ becomes TS, then shall v become QT, and if it dilates so that $\sqrt{\frac{1}{\Delta}}$ becomes UW, then shall v become QU.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

Each point in the positive quarter of the co-ordinate axes represents a medium of a given density and temperature or *vis viva;* the sixth power of the ordinate x represents its density, and the square of its abscissa y its *vis viva.* Thus, $x^6y^2 = e$ is the expression for the tension or elastic force of a medium whose point on this chart (as it may be called) is defined in position by the co-ordinates x, y.

If e is supposed constant, x, y to vary, their *locus* traces out a hyperbolic curve (such as NR) whose equation is $x^6y^2 = e$. It is a curve of constant pressure, of which kind is STPC for one atmosphere drawn on the accompanying large chart of vapours (Plate 1). The sine of the inclination of its tangent to the axis of y is $\frac{1}{3}\,x/y$. Any gas expanding or contracting under a constant pressure traces out a curve of this kind with its varying density and *vis viva.*

It is remarkable that if the points corresponding to the density and *vis viva* of a vapour in contact with its generating liquid are laid down on this chart (fig. 3), they range themselves in a straight line, such as TR, that issues from some point advanced on the axis QC. As this fact applies to all vapours that have been experimented upon, it seems to point to the true physical law of their equilibrium with the liquid. On the accompanying chart of vapours I have projected the points of several sets of experiments. It may be viewed as a portion of the fig. 3 enlarged, the point Q, or origin of co-ordinates, being about 40 inches to the left of the outer margin.

The following details will be sufficient, with the chart, to enable any one to satisfy himself of the truth, and, if he pleases, to construct the formula of any new vapour by means of *two* simple experiments on its tension.

In vapours, as well as gases, the pressure or tension being equal to the product of the absolute temperature or $(t + 461)$ by the density, to find the latter we have only to divide the tabular tension (in inches of mercury) opposite t° Fahr. scale by the former. The sixth root of the quotient is the value of x, and the square root of $(t + 461)$ is the corresponding value of y. In the accompanying chart I have projected several sets of tables of pressures in this way. The unit value of x is $\frac{1}{3}\,10\sqrt{10}$ inches long, and the unit value of y, or square root of absolute temperature, is $\frac{10}{6}$ths of an inch in length.

It will be remarked how nearly the experiments of SOUTHERN and the French Academy on steam range themselves in one line. To observe this more distinctly I have drawn the straight line SF through SOUTHERN's pressure at 212°, and the French Academy's observation at 429·4. The divergence at the four lowermost experiments of SOUTHERN is more apparent than real, the greatest difference being equivalent to only $\frac{3}{100}$ths of an inch of mercury.

The general equation for a straight line TR (fig. 3) is $x = (y - \mathrm{G}) \tan \mathrm{H}$, in which $\mathrm{G} = \mathrm{QT}$ and $\mathrm{H} = \mathrm{RTC}$. Each vapour being represented by such a line with two constants G and H, to find these constants, which may be done by two experiments on any one vapour, let e_0 be the tension at t_0 temperature Fahr., and e_1 the tension at t_1 temperature; then since $y_0^2 = 461 + t_0$ and $y_0^2x_0^6 = e_0$, we have

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

$x_0 = \left(\frac{e_0}{y_0^2}\right)^{\frac{1}{6}} = \overline{y_0 - G} \tan H$, or $\tan H = \sqrt[6]{\frac{e_0}{461 + t_0}} \times \frac{1}{\sqrt{461 + t_0} - G}$; and by 2nd experiment $\tan H = \sqrt[6]{\frac{e_1}{461 + t_1}} \times \frac{1}{\sqrt{461 + t_1} - G}$. From these we eliminate*

$$G = \frac{\sqrt{461 + t^0}\sqrt[6]{\frac{461 + t_0}{461 + t_1} \times \frac{e_1}{e_0}} - \sqrt{461 + t_1}}{\sqrt{\frac{461 + t_0}{461 + t_1} \times \frac{e_1}{e_0}} - 1}. \dagger$$

From the two observations corresponding to the points S and F, I have computed the value of $G = 19{\cdot}4923$ and $\tan H = 0{\cdot}092308$, which define the equation for the steam line that best answers to the experiments of SOUTHERN and the French Academy combined. This equation is $\tan^6 H\,(\sqrt{461 + t} - G)^6\,(461 + t) = e$, or by putting cot H as the common denominator we have the following formula for the tension of steam at all temperatures :—

$$\left\{\frac{\sqrt{461 + t} - 19{\cdot}4923}{10{\cdot}883}\right\}^6 (461 + t) = e \text{ (in inches of mercury).}$$

It is singular that the points of projection belonging to each of the many sets of experiments on steam range themselves in a line, but these lines do not coincide, except in the case of SOUTHERN and the French Academy. Each set is thus consistent with the general law, and on this account their want of accordance with each other is difficult to explain. It might be caused by an error of the standard scales, but this is hardly possible; or impurity of the water, which is not very likely where every precaution has been so carefully attended to. Dr. URE's line of observations is more inclined to the axis than SF, the cot H in the formula being 10·3 and $G = 19{\cdot}8$. The line of the American Institute's experiments has yet a greater elevation, the cot H being about 9·8.

The other lines of vapour on the chart explain themselves. It will be remarked that the deflections from the straight are all of a zig-zag character, there is no general bending to one side or another, and this seems to show that there is some physical law upon which the equilibrium of vapours with their liquids is arranged that is represented by the above function of the temperature. As it seems to apply to all vapours, it is probably not beyond the grasp of physical research, if the *vis viva* theory is admitted, for it evidently does not depend on the chemical qualities of the body any more than does the law of volumes in gases.

It must be confessed that as yet we have but few materials wherewith to found a process of investigation. The fundamental point is the specific heat of steam.

* [? determine.—R.]

† If DALTON and GAY-LUSSAC's constant of expansion is preferred, 448 is to be substituted in the place of 461.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

If it is more than about one-third that of water, if for equal volumes it is not the same as that of air and the other gases, then is the theory incomplete and altogether defective.

It is stated to be about 0·84, but this requires confirmation. The specific heat of the vapour of alcohol ought to be only $\frac{1}{5}$th that of the liquid. The vapour of ether only $\frac{1}{7}$th that of the liquid. Vapour of etherine $\frac{1}{4}$th. Vapour of sulphuret of carbon $\frac{1}{4}$th. Vapour of oil of turpentine $\frac{1}{10}$th. Vapour of bromine $\frac{1}{4}$th, &c.

These are from MM. DE LA RIVE and MARCET'S experiments.

Is there any direct evidence in favour of or against this view? So far as I can discover, little, if any, on either side. It is quite undetermined as yet by experiment, and is so surrounded by practical difficulties that it will probably long remain so.

But analogy favours it in so many ways as to make it highly probable. Liquid etherine has four times the specific heat that its vapour ought to have, judging from its specific gravity. Now, olefiant gas is isomeric with etherine, and its specific gravity is one-half that of etherine vapour. It can hardly be doubted that the specific heat of liquefied olefiant gas for equal weights is the same as that of etherine, which corresponds very nearly with naphtha, turpentine, and the other hydrocarburets. If it is so it will be double what it ought to be, if for equal volumes it is the same as that of air and the other gases. Now, the eminent French chemists who have at different times made experiments on the specific heat of this gas agree that it is nearly 1·5 times that of air, while Mr. HAYCRAFT ('Edin. Trans.'), on the other hand, with his simple and apparently most efficient apparatus, found it to be the same as that of air, and accounts for the higher number of the French chemists by the great difficulty there is in freeing it from ethereal vapours.

It is the same with carbonic acid gas (the only other exception to the law of equal specific heat for equal volumes). The French chemists agree that its specific heat lies between 1·175 and 1·258; Mr. HAYCRAFT, by many experiments, that if carefully dried, it offers no exception to the general law. Judging from the analogy of other similar binary compounds, there cannot be a doubt that the specific heat of liquefied carbonic acid is double, if not three times, that of the gas.

It would be a most valuable addition to our knowledge if this great change in the specific heat of a body when it becomes vapour could be thoroughly established, and it is in vain to proceed with the subject of vapours until it is so.

Sulphuric ether is probably better adapted for the experiment than any other body. Its boiling temperature is very low, and there is a vast disproportion between the specific heat of the liquid and what may be expected in the vapour. Suppose a volume of it and of air are maintained in equilibrium of pressure and temperature by means of a bent tube with mercury. If a sudden small and equal dilatation is made in both at the same instant, the difference of pressure that will then become apparent will indicate the value of the latent heat of the vapour in terms of its specific heat, and, as we know the value of the same in terms of the specific heat of water, we shall have

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

the ratio of the specific heat of the vapour to that of water. The air follows the line RQ (fig. 3) in its expansion, while the vapour is obliged to keep to its line RT.

The latent heat of vapours is another subject where there is room for much additional research. Dr. URE, in his 'Dictionary of Chemistry,' has given a table of eight vapours, but none of the liquids appear to have been pure. The ether boiled at 112°, and the specific gravity of the alcohol was 0·825. If a correction is made for this want of purity, it is singular that the latent heat of each is almost exactly in the inverse ratio of the specific weight of its vapour. This may indicate that the heat required to vaporize a molecule of each of these bodies is the same, and amounts to 3000°, referred to the constant specific heat of a gaseous molecule, which is the proper theoretical standard.

Is this the measure of the force of liquid cohesion? On the *vis viva* theory of heat this, for 1 lb. of water, amounts to the force required to raise 1 lb. to the height of about 680,000 feet. According to MITSCHERLICH, the *vis viva* generated by the union of the constituent elements of the same quantity of water amounts to ten times this force.

Considerable attention has lately been given to thermo-chemistry; but it is to be regretted that no notice has been taken of the permanent change of specific gravity that is usually found to ensue in chemical mixtures that evolve heat. It would be interesting to ascertain if there is any harmonious connection between the quantity of heat evolved and the change of atomic volume. Dr. URE has given a curious example of hydrated nitric acid, where the permanent change of volume appears to be the same as would be caused by a permanent change of temperature equal to the heat evolved.

Since only two experiments are required to fix a line of vapour on the chart, it would not be a very arduous undertaking to accomplish this for all bodies that throw off vapours at accessible temperatures. We might then have the means of answering the various questions that cannot fail to suggest themselves on looking at the chart; and, first of all, do the vapours of arsenic, iodine, camphor, salts of ammonia, and the other solids that rise into vapour before becoming liquid, follow the general law? This question has yet to be determined.

How are the lines of vapour of the simple bodies related to each other? We have only one example as yet, viz., the vapour of mercury by M. AVOGADRO. It will be remarked that the line drawn through MR, the third and the second last observation, agrees very well with the position of the other points. This line produced meets the axis at 50°, which is certainly lower than the temperature assigned by Dr. FARADAY's delicate experiment as the point of no vapour. In judging of this discrepancy, however, we must recollect that the density is represented not by the ordinate to the line of vapour, but to its sixth power; hence, at the temperature of 75°, the density indicated by the line on the chart is only $\frac{1}{120,000,000}$th of the

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

density of an atmosphere. The formula that corresponds to this line has the constant $G = 22{\cdot}6065$ and $\cot H = 20{\cdot}0023$.

It will be remarked that the line for DALTON's ether (which, from its low boiling point, must have been nearly pure), THOMPSON's pyroxilic spirit, and the well determined line for steam, are nearly parallel; is this parallelism perfect? It is also remarkable that the projection of two experiments by DALTON on aqueous ammonia is exactly parallel with the steam line, and further, that the same parallelism is maintained by the vapours of liquefied ammoniacal gas and carbonic acid (by THILORIER). It would be extremely desirable if Dr. FARADAY's experiments on chlorine and the other more condensible gases could be repeated on a large scale so as to determine their position on the chart, and by two or three observations on each to eliminate the constants G and H. It is by such experiments and those of M. CAGNIARD DE LA TOUR, made at the other extremity of the scale of heat and pressure, and likewise by Mr. PERKINS, all of which may be classed under the head of chemical physics, that we may expect to extort from nature some of her most hidden secrets, to come in sight of new continents in the world of natural science, not dreamt of in our philosophy, because removed beyond the bounds of suggestive analogy. Such pressures appear to us great, and are certainly dangerous to operate with, but in respect to those which exist in nature, and that everywhere surround us, restrained by internal forces, they can only be considered as infinitesimal.

Note C.—Temperature of Compressed Air.

These changes of temperature are certainly much greater than are said to have been observed by DARWIN, DALTON, and others. Not having access to the original account of these experiments, I am unable to ascertain how far they accord with the theory; but the specific heat of air is so small in comparison to that of the materials of which thermometers are composed that the actual difference of temperature in a single condensation or dilatation must be much greater than what is indicated by any thermometric apparatus.

A more effectual way of ascertaining this seems to be by continually and quickly repeating the same condensation with different portions of air, so that after some time, by proper care, the condensing syringe ought to exhibit the temperature of the air at its maximum tension.

If air is a medium we have in XVI. the means of computing the temperature that ought to be shown by a thermometer placed at the bottom of the syringe.

Thus, t_0, e_0 being the temperature and tension of the air outside, e_1 the tension corresponding to the load on the eduction valve of the syringe; then $\frac{e_1}{e_0} = \left(\frac{t_0 + 461}{t_1 + 461}\right)^4$, and $\left(t_0 + 461\right) \sqrt[4]{\frac{e_1}{e_0}} - 461 = t_1$, the temperature of the air when condensed.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

The air engines of the atmospheric railway may perhaps afford the means of testing this equation.

Note D.—To find the Compression that Corresponds to a Given Ratio of Latent to Sensible Heat.

This may be computed by means of IV. and XVI.

Suppose the medium is compressed so that the mean molecular distance changes from 1 to $\frac{x}{x+1}$, th *vis viva* increases from 1 to $\frac{x+1}{x}$ (XVI.), the increment being $1/x = \mathrm{L}$.

By withdrawing molecular *vis viva* under a constant pressure, let the mean distance change from 1 to $\frac{x}{x+1}$; the molecular *vis viva* must be diminished from 1 to $\left(\frac{x}{x+1}\right)^3$ (IV.), the decrement being $\frac{(x+1)^3 - x^3}{(x+1)^3} = \mathrm{K}$. The ratio K/L is given to find $\left(\frac{x+1}{x}\right)^3$, which is the amount of compression from unity that makes the ratio between the sensible and latent, or evolved *vis viva*, equal to K/L.

If we put $x/(x+1) = y$, the equation resolves itself into $y^3 + y^2 + y = \mathrm{K/L} = \frac{8}{3}$ in the case given. This equation may easily be solved by inspection of a table of square and cube numbers. $1/y^3$ is the compression from unity to give the ratio K/L of the sensible to the latent heat.

Note E.—Specific Heat of Air.

It is probable that the specific heat of mercury and water are better determined than that of any other bodies. Assuming that the specific heat of liquid mercury (0·033) is the same as that of its vapour, and that all gases and vapours have for the same volume the same specific heat when *in equilibrio* of pressure and temperature, the specific heat of air in terms of that of water is 0·238. The mean experimental value is, according to the French chemists, 0·267. Mercury is thus the only liquid, so far as is known, whose specific heat is the same as what it ought to be in the state of vapour, if it conforms to the general law. Water is nearly three times greater than steam ought to be. Alcohol five times that of its vapour. Ether seven times, &c.; see Note B.

This accordance of the specific heat of mercury with its vapour seems to prove that there is little or no part of the heat required to raise the temperature of the liquid absorbed in a latent form. This is an important point in the *vis viva* theory.

It is remarkable that there is no instance, so far as yet known, of mercury combining in fractional parts of a volume. Arsenic, sulphur, phosphorus, and some others combine in fractional volumes, and their specific heat in the form of vapour by

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

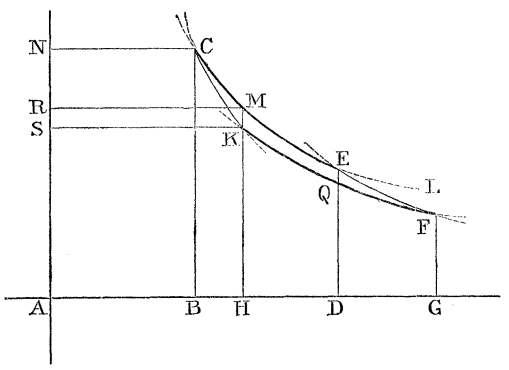
the theory of gases is the same fractional part of the specific heat of the solid. This is somewhat confirmatory of the theoretical interpretation of the law of volumes (§ 15). The vaporous molecule of mercury is indivisible. The vaporous molecule of arsenic is divisible into four parts: of sulphur into six parts; of phosphorus into four parts; of hydrogen into two parts; of oxygen into two parts; of water ($O_{\frac{1}{2}}2H_{\frac{1}{2}}$) into three parts; of alcohol ($2(HC_{\frac{1}{2}}) + 2H_{\frac{1}{2}}O_{\frac{1}{2}}$) into five parts; of sulphuric ether ($4(HC_{\frac{1}{2}}) + 2H_{\frac{1}{2}}O_{\frac{1}{2}}$) into seven parts; sulphuric acid, anhydrous ($3O_{\frac{1}{2}} + S_{\frac{1}{6}}$) into four parts; etherine $4(HC_{\frac{1}{2}})$ into four parts, &c. We may thus predict the specific heat of pyroxilic spirit to be 0·83, and of pyroxilic ether 0·72.

Note F.—M. Clapeyron's *Fundamental Position.*

The density and tension of a medium expanding according to Marriotte's law, are represented linearly by the co-ordinates to the common hyperbola CMEL referred to its asymptote AG; the abscissa AB, &c., representing the volume, and the ordinates BC, &c., the tension.

We have shown that each incremental expansion is made at the expense of the molecular *vis viva* of the medium, so that to maintain the expansion, according to Marriotte's law, the loss of *vis viva* must be continually made up; and the amount required to be supplied for any given expansion, as from B to D, is to the constant

Fig. 4.



original amount as the area CEDB is to 3 CB.AB, or to the original tension CB acting through three times the original volume AB (XIII.).

Suppose the medium to expand from B to H (against pressure) without having its loss of *vis viva* supplied; then, according to § 22, its tension from CB, or unity, becomes $KH = \left(\frac{AB}{AH}\right)^{\frac{4}{3}} CB$. Assuming the original volume and tension as unity and $BH = y$, we have $KH = x = \left(\frac{1}{1+y}\right)^{\frac{4}{3}}$ and $x\,dy = dy\left(\frac{1}{1+y}\right)^{\frac{4}{3}}$ = the differential of the asymptotal area CKHB.

To integrate this put $\frac{1}{\Delta^3} = 1 + y$, and differentiating gives $dy = -\frac{3d\Delta}{\Delta^4}$; and since

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

$x = \left(\frac{1}{1+y}\right)^{\frac{4}{3}} = \Delta^4$, we have $\int x\,dy = 3 - 3\Delta = 3 - \frac{3}{(1+y)^{\frac{1}{3}}} =$ area CKHB in terms of ABCN unity. In this, y being made infinite, we have the area of the whole asymptotal space = 3ABCN, which accords with § 19, as the asymptotal area represents the collective force of expansion from the original volume to infinity.

If, during the expansion from B to H, *vis viva* were supplied to the medium so as to maintain the original quantity unimpaired, the point K in the hyperbola $x = \left(\frac{1}{1+y}\right)^{\frac{4}{3}}$ would coincide with M, the point in the common hyperbola $x = \frac{1}{1+y}$, or MH $= \frac{\text{AB}}{\text{AH}}.\text{CB}$. Now, it is evident that MH : KH : : $\frac{1}{1+y} : \left(\frac{1}{1+y}\right)^{\frac{4}{3}}$: : 3 : $\frac{3}{(1+y)^{\frac{1}{3}}}$; but the preceding integral gave $\frac{3}{(1+y)^{\frac{1}{3}}}$ = 3ABCN − CKHB, therefore MH : KH : : 3AB.CB : 3AB.CB − CKHB = ratio of original *vis viva* of the medium to the force remaining after expansion from B to H. Thus, MH : MK : : original *vis viva* : decrement of *vis viva* owing to expansion; and three times the area KNAS is equal to the asymptotal area on the other side of KH. These relations evidently hold good in whatever part of the conic hyperbola the point C may be taken.

Suppose the medium is maintained at its original *vis viva* while it expands from C to E, it will exert the mechanical force CEDB $= p$, and absorb the *vis viva* CEDB, the original quantity in the medium being 3AB.CB. From E let it expand to F without being supplied with *vis viva;* then, as before, FG $= \left(\frac{\text{AD}}{\text{AG}}\right)^{\frac{4}{3}}.\text{ED}$ and $\frac{\text{LF}}{\text{FG}}$ is the proportion of original *vis viva* expended represented by EFGD $= (m)$, its equivalent mechanical force exerted. Let it now be compressed from F to K, the *vis viva* communicated to the medium being continually withdrawn. The amount withdrawn and the force exerted is represented by the area FGHK $= q$. From K let the medium be compressed without withdrawing the *vis viva* generated until the original tension CB and density AB are regained. The force of compression and *vis viva* communicated to the medium in the last operation is represented by the area CKHB $= n$. For shortness put the area KQDH $= s$, CEFK $= \delta$, and EQF $= \epsilon$. It is evident since the molecular *vis viva* through CEL is constant and through KQF constant, that $\frac{\text{LF}}{\text{LG}} = \frac{\text{MK}}{\text{MH}}$ and $\frac{\text{MH}}{\text{LG}} = \frac{\text{MK}}{\text{LF}}$. Also, $\frac{\text{MH}}{\text{LG}} = \frac{\text{AG}}{\text{AH}} = \frac{\text{MK}}{\text{LF}}$, or AG.LF = AH.MK = SK.MK $= n = m$. But $q + e = s + m = s + n$, and $s + n + \delta - \epsilon = p$. In this equation substitute for $s + n$ its equal, $q + e$, and we have $q + \epsilon + \delta - \epsilon = q + \delta = p$. Thus, the curvilinear area δ, or CEFK, is the excess of the force exerted by the medium expanding from C to E at the higher constant temperature, over the force exerted upon the same, compressing it from F to K at the lower constant temperature. It is also the excess of the *vis viva* absorbed in the first part of the process over the *vis viva* given out in the last part.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

This is the interpretation of M. CLAPEYRON's fundamental position* applied to the hypothetical medium. M. CLAPEYRON assumes that the quantity of heat taken from the body A (p. 349, 'TAYLOR's Memoirs') during the expansion from C to E is necessarily equal to the quantity given to the body B during compression from F to K, and that from E to F and K to C *no* heat is taken from or given to the volume of gas, a proportion only of the sensible heat being reduced to a latent form and again thrown out. Thus, there appears the anomaly of the mechanical force δ being exerted or generated without any loss of heat. M. CLAPEYRON's view is here so much at variance with the *vis viva* theory of heat that it seemed proper to enter into a full explanation of the same condition in the hypothetical medium. The case is very instructive, and throws light on the *vis viva* theory, which is at the same time the means of clearing up the anomaly in causation of mechanical force seeming to be generated without expenditure of heat. M. CLAPEYRON's conclusions, so far as gases are concerned, are quite independent of any hypothesis, and seem to be strictly deduced from the laws of MARIOTTE and DALTON and GAY-LUSSAC combined with the relation that has been found to subsist between simultaneous increments of sensible and of latent heat. It is satisfactory to observe that they agree, so far as they go, with the physical properties of the medium.

Note G.—Objection to Theory.

The only difficulty I can discover in the *vis viva* theory of heat applies in some measure to the undulatory theory of light. The ethereal medium that transmits the undulations is affected by vibrations of the elements of matter, but there is not the least symptom of it affecting by its resistance the planetary motions, and yet theory shows that it must permeate through the very substance and heart of all bodies with such quick and subtle power as not in any sensible manner to be affected in its equilibrium by any part of their motion except what is vibratory. Now, the *vis viva* theory of heat shows that the greatest ordinary velocities of this vibratory motion do not much exceed 2000 feet per second, but the velocity of the earth in its orbit is upwards of 50 times this amount. In the first case, if a hot body were isolated from all surrounding matter, the whole of its motion would be withdrawn from it in a very short time by the ethereal medium. This we can affirm inductively from the laws of the radiation of heat. In the second case not the slightest resistance is made manifest. The ether only affects and is affected by vibratory motion. Any other kind, however great, it neither affects nor is affected by. What are we to infer from this incongruity? If vibratory motion differed in no other point from the rectilinear and rotatory motion of masses of matter, than in the sudden change of direction, it is plain that if there was no resistance in the one case there could be no resistance in the other, and *vice versâ*. We are, therefore, compelled to infer that the disturbance

* Essay on the motive power of heat, 'Journ. Polyt.,' translated in 'TAYLOR's Memoirs,' vol. 1, p. 349.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

of the ethereal medium is not caused directly by the motion of material particles as with the grosser media of gases and liquids when affected by the motion of bodies passing through them. Something takes place in the vibratory motion of the elements of matter that does not take place in their collective motion.

Molecular vibration consists in the struggle, as it were, between the *vis insita* of molecules and the forces that bind them together. It seems, therefore, as if the disturbance of the medium which answers to radiation of heat and light were derived from the disturbance of the molecular forces, and that when there was no such disturbance there was no resistance.

But the difficulty yet remains of a body moving in a material medium without resistance. It is almost inconceivable in the present state of our knowledge of molecular physics. If it is at all possible (for there is almost an absurdity involved in asserting that it is possible) it can only be by means of a persistent or continuous relation of intense mutual organized activity between the ether and the perfectly elastic elements of matter, of which we can as yet have very little conception.

The disturbance of molecular forces that allows the medium to absorb the *vis insita* of vibrating molecules may be likened to the ascent and descent of planetary bodies to and from the sun while revolving in elliptic orbits. There is a disturbance when the centripetal force on a body increases or diminishes, so that if a body revolved in a circle there is no disturbance, no resistance, no absorption of its *vis insita* by the active medium, and if it revolves in an eccentric ellipse there is disturbance, resistance, and absorption. The number of luminous vibrations in a second is, by the undulatory theory, from 458 million million to 727 million million, and the vibrations that cause heat are probably not very different in the velocity of their succession. If a set of molecules thus vibrating in a perfectly cold region took one second to dissipate their molecular *vis viva* by radiation, this is sufficient time for so vast a multitude of revolutions in the molecular orbits that the loss of *vis insita* in our vibration is probably as infinitesimal as that of the planets during one revolution, and we might conjecture that this infinitesimal ratio was a function of the ratio of the elasticity of the ether to the molecular velocity of the vibrations, the elasticity of the ether being apparent only as an active centripetal force. Such a retardation would certainly follow if the velocity of the action of gravitation were not infinite, but there still remains to be suggested the physical condition of a medium that offers no resistance. Is such an entity possible?

Note H.—Formula for Measuring Heights by the Thermometer.

The tension of the atmospheric medium varies, as we have seen, in the proportion of the sixth power of the depth below the summit, and the elasticity of steam varies as the sixth power of the ordinate to the line SF on the chart multiplied by the absolute temperature or square of the corresponding abscissa (see Note B). This

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

suggests a method of measuring heights by the thermometer that requires little or no computation.

Let ST on the chart of vapours, which there represents the sixth root of the density of steam at 212°, be also taken to represent the whole height of the atmosphere above a point where the water boils at the temperature of 212°. Then from ϖ, the ordinate to the steam line at 200°, draw ϖq parallel to QS, the line of one atmosphere pressure, or rather, it ought to be converging to the point where the cord QS produced meets the axis. It is evident that SQ represents very nearly the height where water boils at 200°. Now, if such lines are drawn at each degree between 200° and 212°, they will divide Sq into parts that are sensibly equal.

The value of each of these parts depends on the value given to ST, which, according to our theory, is in feet 318 times the absolute temperature of the air at the station where water boils at the temperature corresponding to the square of the abscissa of the ordinate ST.

The following is the accurate formula by the theory for any vapour of which the constant G (see Note B) is known :—

$$317{\cdot}6\left\{1-\left(\frac{\sqrt{\tau+461}-\mathrm{G}}{\sqrt{t+461}-\mathrm{G}}\right)\left(\frac{\tau+461}{t+461}\right)^{\frac{1}{8}}\right\}(\mathrm{T}+461)=h,$$

in which T is the temperature of the air at the lower station, t = temperature at which the liquid boils at the lower station, τ = temperature at which the liquid boils at the upper station (all expressed in degrees on Fahr. scale), G the first constant of the vapour (see Note B), and h the difference of height between the stations in feet. By boiling temperature is meant the temperature at which the tension of the vapour is the same as that of the external atmosphere.

Let us apply the formula to the vapour of water, in which G is 19·4923, and let us take an example where T is 60°, $t = 212°$, and $\tau = 211°$; the value of h is 528·6 feet. It will be found, by taking other values for T and τ, that this elevation for 1° difference in the boiling point increases about $\frac{7}{6}$ths of a foot for each degree that τ diminishes, and increases exactly 1 foot for every degree that T increases, and *vice versâ*.

Professor FORBES, who has discussed this subject fully in a recent paper, finds that his observations indicate a number between 540 and 550 feet. The accordance is thus satisfactory; by the formula, 550 feet per 1° is the mean value for T = 75°, $t = 212°$, $\tau = 202°$, which corresponds with Professor FORBES' mean; and what it wants of uniformity is too small to be discovered in practice.

Suppose that we wished to employ the vapour of sulphuric ether for this purpose. It boils at 96° under a pressure of 30 in. DALTON'S observation on this ether gives a line of vapour which has G = 16·86. Compute the above equation with this value of G, and $t = 96°$, $\tau = 95°$, T = 60°. The result is $h = 568$, being $\frac{1}{13}$th greater than in the former case of steam.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

The less this ratio, the more exact, of course, is this method of estimating heights, and it depends greatly on the value of the constant H (see Note B), for the less the inclination of the line of vapour is to the axis the smaller is the height that corresponds to a difference of 1° in the boiling point. For mercury this is only 248 feet, but the temperature is inconveniently high.

Pure sulphuric ether appears to be the best adapted, as its boiling temperature is low, and the disadvantage of the great amount of the difference of elevation for 1° might, perhaps, be compensated for, by employing a very delicate alcohol thermometer, with the divisions of the scale large and extending only from 60° to 100°. The ether need not have access to the air; the equilibrium of pressure may be indicated by the rising of a thin metallic capsule air-tight and elastic.

Such an instrument would require little more than the heat of the hand to bring it into action, and perhaps might be made sufficiently delicate to be used as a machine for taking levels and making sections of a country.

Note K.—Central Heat.

It is not difficult to compute the temperature that the atmosphere would have if it were supposed to be continued through a shaft to the centre of the earth. Suppose the force of gravity to diminish with the central radius, which is the case in a homogeneous sphere, the temperature of the air at the centre would be about 29,000°, and the density much greater than that of any known solid.

Heat, if it is motion, cannot be propagated upwards without loss or conducted downwards without gain, any more than can a body when projected upwards retain its original velocity without diminution, or when projected downwards without increase.

The temperature in mines (according to M. CORDIER) increases in descending at the rate of 1° to 50 or 60 feet. Is this the natural condition of vertical equilibrium of molecular *vis viva* within the crust of the globe? If such were the case some regular difference might be found between the top and bottom temperatures in pillars or lofty buildings if precautions could be taken to prevent horizontal conduction.

Note L.—Nebular Hypothesis.

The *vis viva* theory appears to harmonize well with the Nebular Hypothesis of LAPLACE. The intense activity of the molecules of the Sun's mass may be viewed as the result of, or to have been originally produced by, its centripetal force while condensing. The motion generated is not lost, as it is in appearance when inelastic bodies meet each other with equal momenta. The clashing together of the descending elastic matter is followed by equal recoil in the opposite direction, and molecular *vis viva* is generated. We see this take place on a minute scale when metals are

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

hammered, or compressed, or rubbed. Friction and every other expenditure of mechanical force gives birth to heat or molecular *vis viva*, which is dissipated by radiation and conduction.

The observations of Sir JOHN HERSCHEL and Professor FORBES with the actinometer ('Phil. Trans.,' 1842) have recently supplied a knowledge of the absolute value of the solar radiation before it passes through the atmosphere. They have found it to amount to 388·4 actines, each actine being one-millionth of a metre in thickness of ice melted per minute. This is equal to 1·835 ft. of ice melted in a mean solar day.

Now, since it is known that ice requires 140° of heat to melt it, and the mechanical value of 1° in water is equal to the weight of the water raised through 673 feet against the force of gravity on the Earth's surface (§ 25), we have the means of computing exactly the absolute mechanical power of the solar radiation—the absolute force thrown out by the Sun in a given time.

There are various ways of reckoning this and obtaining a clear conception of it with reference to different standards. The fundamental principles are contained in Section 3, and an example of their application is given in detail in § 25. The results of four computations are as follows :—

1. During one year the solar force upon a square foot at the Earth's mean distance from the Sun is equal to 20 tons raised 20 miles, or to about one ton raised one mile per day, which is equivalent to $\frac{1}{4}$th of a horse-power, according to engineers' mode of reckoning.

2. At the Sun its amount in one year is equivalent to the descent of a stratum of the Sun's surface (and of its mean density) $3\frac{1}{3}$ miles thick through its own breadth.

3. If the Sun is supposed to contract uniformly throughout its mass so that its radius becomes $3\frac{1}{3}$ miles less in consequence of the general increase of density, the force generated is sufficient to supply the solar radiation for about 9000 years.

4. If a mass equal to the Earth descended to the Sun's surface from its mean distance, it would acquire a velocity of 390 miles per second, and the *vis viva* generated when it strikes the Sun would amount to the force thrown out by the Sun in 45 years.

The density of the Sun being little more than that of water, it is possible that the mere gradual contraction of its bulk, or natural subsidence of the mass, may generate sufficient force to supply the amount of radiation without any diminution of temperature, and it would appear from the third computation that the decrement of the apparent diameter of the Sun owing to such condensation may not amount to more than $\frac{1}{50}$th of a second in 9000 years.

Note M.—Barometric Formula.

This may include the effect of aqueous vapour by the formula in Note B. Let τ = mean dew point, t = mean temperature of the air at the two stations. Find

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

$$P = \left\{\frac{\sqrt{\tau + 461} - 19{\cdot}736}{10{\cdot}422}\right\}^6 (t + 461),$$

then

$$H = (\log B - \log b) \cdot \frac{1250801}{1 - 0{\cdot}376\left(\frac{2P}{B + b}\right)} \cdot \left(\frac{461 + t}{9958 + t}\right)$$

is the correct theoretical formula, in which

H = height in feet between the two stations.

B = height of barometer at lower station.

b = height of barometer at higher station brought to the same temperature as B.

Addition to Notes B. *and* H. *of the Paper, "On the Physics of Certain Media," recently submitted to the Royal Society.*

Received January 27, 1846.

In Note B it was shown that the formula of a vapour might be obtained from two experiments on its tension, and in Note H, that the function which defines the law of density in vapours is analogous to what defines the law of tension in ascending the atmosphere, thereby enabling us to construct a rule for measuring heights by the thermometer. It may, perhaps, be useful to add what relates to the law of the tension of mixtures of air and vapour.

In some cases it seems impossible to clear vapours entirely of permanently elastic matter, and it will be allowed to be very desirable, in a practical point of view, that we should be able to deduce the necessary constants from experiments made upon them in their usual state of commixture. It will be found, I believe, that this may be accomplished by means of the data afforded by not less than three experiments if the volume occupied by the gas and vapour remains constant, or if the proportionate changes in it are capable of being accurately determined. We do not require to know anything of the quantity of air enclosed with the vapour: this forms one of the three unknown quantities involved in the three equations afforded by the experiments; the other two being the constants G and H that develop the law of density of the pure vapour.

In the accompanying chart (Plate 2), which is drawn on the same scale as the general chart of vapours given in Note B, it may be remarked how the straight lines of vapour are transformed into a high order of hyperbolas when any permanently elastic matter is allowed to contribute its effect of tension. The mode of laying off the points is simply as follows. Suppose we wish to know the effect that air of $\frac{6}{100}$ths of an inch of tension at 51° has upon the chart line of aqueous vapour; we have $F^6 t = F^6 (51 + 461) = 0{\cdot}06$. From this we obtain the value of F^6, which we employ in the general equation for such mixtures, viz., $F^6 t + t\left(\frac{\sqrt{t} - G}{H}\right)^6 = e$, or $\sqrt[6]{F^6 + \left(\frac{\sqrt{t} - G}{H}\right)^6} = \sqrt[6]{\frac{e}{t}}$ = the ordinate

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

on the chart to the abscissa $\sqrt{t}$. The curve traced out by these coordinates is one leg of a species of hyperbola. The apex of this hyperbola has its ordinate F′F′ (see chart) equal to the element F in the equation, and the corresponding abscissa is G, which is equal to $\sqrt{t}$ at this point which is the zero of the vapour. It makes $\frac{\sqrt{t} - G}{H} = 0$, and $\sqrt[6]{\frac{e}{t}} = F$.

As the tension of a vapour is excessively small for a considerable range of temperature above its zero point, the curve, which begins at F′, does not sensibly leave the tangent at its vertex, F′E,—which is also parallel to the axis at the distance from it, F,—for some distance beyond the point of contact. It then takes a sudden bend, having the greatest curvature at the point where the tension of the vapour is nearly one half the tension of the air, and ascends along the line of vapour converging towards it as an asymptote. This curve answers very well to the general run of the experiments on aqueous vapour at low temperatures, and those of Professor MAGNUS that have recently appeared in the 14th number of the 'Scientific Memoirs' correspond with it almost exactly.

Are we then to infer from this coincidence that the general divergence from the straight at low temperatures is the effect of a minute portion of air that clings to the water, in spite of all the precautions taken to prevent it, and that it only becomes sensible when the tension of the vapour, *per se*, has descended to the same attenuated proportion; or is the law that is represented by the general equation of Note B, defective to this trifling extent?

Although no attempt has yet been successful to give a physical interpretation of the function of the temperature that represents the density of a vapour, yet it must be considered as a circumstance favourable to the possibility of doing so on the *vis viva* theory, that it corresponds so far with several of the laws of gases or media as like them to involve the sixth power of an element of the temperature. Thus in XVI. (§ 22) it was shown that when a medium was compressed the *vis viva* increased as the mean molecular distance diminished, or, what is the same, that the sixth power of the molecular velocity increased in the same ratio as the density. This actually enables the condition of a gas in respect to density and temperature, while dilating or being compressed, to be represented on the chart of vapours, and has already been referred to in Note B. The physical demonstration of this peculiarity of function depends ultimately (as shown in Section III.) on the six rectangular directions of space. It seems highly probable, therefore, that the same primary cause shapes the function in the case of vapours, and we may thus be led to hope that in the liquid condition of bodies their molecules are arranged upon a plan more simple and less interwoven with the essential nature of the molecular forces than might otherwise have been anticipated.

In the upper curve, FCS, the ordinates represent the sixth root of the respective

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

densities when the air and vapour are in equal proportion at the ordinary pressure of the atmosphere. The vapour is that of the sulphuret of carbon employed by M. MARX* ('Scient. Mem.,' Part 14), which has 117°·12 as its boiling temperature. With half its volume filled with air it assumes the ordinary pressure of the atmosphere (30 inches) at 80°·55. At this point it crosses the line of the constant pressure of one atmosphere (see Note B) as may be seen on the accompanying chart. It may also deserve to be remarked that the curve crosses this line in a much more sloping direction than the straight line of the pure vapour, and that, consequently, according to what is stated in Note H, such a mixture is so much better adapted to the measurement of heights by the thermometer, inasmuch as 1° represents a much less difference of height in the atmosphere when applied to mixtures of air and a vapour, than with the same vapour in its pure state. We may thus, perhaps, with such mixtures, be enabled to construct an instrument for measuring heights by means of the thermometer which will have all the advantages that are anticipated in Note H from employing the pure vapour of a volatile liquid with a chart line of density having the smallest possible inclination to the axis.

As an example of this let us take the mixture represented by the upper line of density, FCS.

At the temperature 80°·55 and the mercury in the barometer standing at 30 inches, a small quantity of air saturated with sulphuret of carbon is enclosed and at the lower temperature, 70°, the tension of the mixture of air and vapour reduced to 26·76; it is required from these data to determine the height corresponding to a lowering of 1 degree in that temperature which brings the tension to an equilibrium with the external atmosphere.

We have first to compute G by the formula given in Note B as follows:—

$$G = \frac{\sqrt{t_0}\sqrt[6]{\frac{t_0 e_1}{t_1 e_0}} - \sqrt{t_1}}{\sqrt[6]{\frac{t_0 e_1}{t_1 e_0}} - 1};$$

in which $t_0 = 461 + 70$, $t_1 = 461 + 80{\cdot}55$, $e_0 = 26{\cdot}76$, $e_1 = 30{\cdot}00$.

By this we obtain $G = 8{\cdot}742$. It is making use of the small arc, CS, as if it were a straight line.

We have next to employ the value of G in the formula of Note H, viz.:—

$$317{\cdot}6 \left\{1 - \left(\frac{\sqrt{\tau} - G}{\sqrt{t} - G}\right)\left(\frac{\tau}{t}\right)^{\frac{1}{6}}\right\} \cdot T = h.$$

In this the absolute temperature at the lower of two stations is denoted by T, and t is the temperature at which the tension of the enclosed air and vapour equilibrates the atmospheric pressure at the lower station, the same at the upper station being τ.

* [? Magnus.—R.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

Suppose

$$T = (461 + 60), \quad t = (461 + 80{\cdot}55), \quad \text{and} \quad \tau = (461 + 70);$$

the formula computed gives $h = 3127$, which, divided by $t - \tau = 10{\cdot}55$, gives $296\frac{1}{2}$ feet as the value of 1° in such an instrument. This amount varies but little, through a considerable range of temperature and pressure.

This value may be obtained by observing the temperature at the bottom and at the summit of a known height, and dividing the elevation in feet between the two stations by the difference. Neither the law of the vapour nor the amount of air enclosed with it is required.

What if we dismiss the vapour altogether and enclose dry air only? It is evident that the line CS will then become parallel to the axis and distant from it F, the sixth root of F^6, the density, which is constant. The element G becomes infinitely negative, and $\frac{\sqrt{\tau - G}}{\sqrt{t - G}} = 1$, thus simplifying considerably the expression for h, which is now converted into $h = 317{\cdot}6 \left\{1 - \left(\frac{\tau}{t}\right)^{\frac{1}{6}}\right\} T$.

Let $t = b^6$, and $\tau = (b - \beta)^6 = b^6 - 6b^5\beta$, when β/b is a small fraction. By division we have on this hypothesis $\tau/t = 1 - 6\,\beta/b$, and $(\tau/t)^{\frac{1}{6}} = 1 - \beta/b$, which converts the equation for h into $h = 317{\cdot}6\,\frac{\beta}{b}\,T$. To express $\frac{\beta}{b}$ in terms of t and τ, we have $\overline{t - \tau} = 6b^5\beta$, and $\frac{t - \tau}{6t} = \frac{\beta}{b}$. Hence, so long as this fraction is small in comparison to unity, we have the following simple expression for the height in terms of the indications of the thermometer:—

$$h = 317{\cdot}6 \left(\frac{T}{t} \cdot \frac{t - \tau}{6}\right).$$

This gives the nearly constant value, 53 feet, for each degree of Fahr. thermometer, at moderate elevations and ordinary temperatures.

This is the lowest possible value for difference of temperature that can be obtained. In ascending through an increment of the height of the atmosphere, we experience one decrement of temperature, and five decrements of density, which, together, make six decrements of tension. These six decrements of tension must be effected in the enclosed air of the instrument before an equilibrium is established, and as the density is a constant quantity they must be produced by means of a lowering of temperature to the amount of six decrements. Thus, six decrements of temperature in the instrument correspond to the same differential height as one decrement of temperature in the atmosphere, or six degrees correspond to 317·6 feet, the difference of height that causes a difference of 1° while in its natural condition of vertical equilibrium.

It appears, therefore, that dry air is in every respect the best in theory for measuring heights with the thermometer by means of such an instrument as is referred to in Note H. The theory upon which its theory rests has been shown to agree with

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

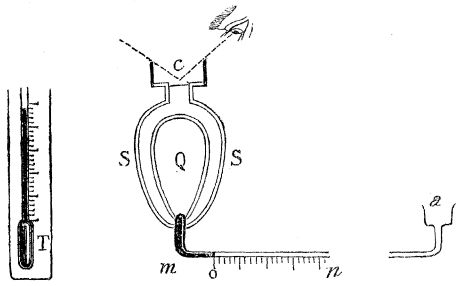
M. GAY-LUSSAC'S observations during his balloon ascent, § 34, and also with Professor FORBES'S original determination of the nearly constant difference of level in the atmosphere that corresponds with the same constant difference in the boiling point of water.

Suppose, then, we take a small glass vessel, in which there is fixed a delicate thermometric apparatus with a large scale. We heat it to about 100°, and the inside being perfectly dry we close it and make it perfectly air-tight by means of a thin, finely polished silver capsule. From 100° down to 60° corresponds to an altitude of only about 2100 feet, so that for greater elevations or a greater range of the barometer we would require to seal it at a higher temperature, or what amounts to the same thing, partially exhaust the air while fixing the capsule. In afterwards employing this instrument the polished capsule will be a concave mirror so long as the pressure of the atmosphere exceeds the tension of the enclosed air. It will become a plane reflector when they are in equilibrium, and convex when the tension exceeds the atmospheric pressure.

Now, the image of an object is so different in these three kinds of reflectors, that I conceive it will be possible to recognise the point of equilibrium with very considerable accuracy, or, perhaps, better by means of an eye-piece adjusted to a certain angle of reflection.

The principal difficulty in such an instrument would probably be in getting the temperature of the air and of the thermometer to be perfectly the same at the instant of equilibrium. M. BREQUET'S metallic spiral thermometer is, perhaps, the best adapted, and would make the apparatus very portable. But it is the practical artist only who can judge if such an instrument can be made effective.

Fig. 5.



The annexed sketch is another form of the apparatus, to be used with a delicate mercurial thermometer that may show the temperature of the atmosphere at the station. Q is an air thermometer, with a bead of mercury as index, which, before observing with it, must be blown into the bulb by putting the finger upon the open end, *a*.

The air in Q, having now the same temperature and density as the atmosphere outside the bead of mercury, is allowed to fall into the stem of the instrument, and

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

the reading of the scale marked off. Heat is then applied to the shut glass bottle, SS, that encloses Q, until the capsule, C, shows the equilibrium; the air in Q, of course, has the same temperature, and has expanded accordingly against the constant pressure of the external atmosphere; the reading of the mercury in the scale, n, will now show the amount of expansion, and, therefore, the ratio of the constant density of the air enclosed in SS to the density of the atmosphere at the station. Thus, we ascertain the absolute temperature and absolute density of the atmosphere at every station from scales with as large a reading as we please.

To obtain the law of tension of a vapour by three experiments made upon it at different temperatures when mixed with an unknown quantity of air, let t_0, t, t_1 be the three absolute temperatures found by adding 461 to the reading of Fahr. scale, and e_0, e, e_1 the corresponding tensions. Also, let G and H represent the two unknown constants of the vapour, and F^6 the constant that represents the quantity of the enclosed air, or number of gaseous molecules, which is the same at all temperatures, while the number of vaporous molecules $\left(\frac{\sqrt{t}-G}{H}\right)^6$ changes with the temperature t. These expressions mean the number of molecules in a constant volume, so that the experiments require to be made with the enclosed volume over the liquid constant. The general expression for the observed tension is

$$e = t\,F^6 + t\left(\frac{\sqrt{t}-G}{H}\right)^6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

By eliminating F^6 from each of the three experiments, we have

$$F^6 = \frac{e_0}{t_0} - \left(\frac{\sqrt{t_0}-G}{H}\right)^6 = \frac{e}{t} - \left(\frac{\sqrt{t}-G}{H}\right)^6 = \frac{e_1}{t_1} - \left(\frac{\sqrt{t_1}-G}{H}\right)^6 \quad . \quad . \quad (2).$$

From the first and second of these, we have

$$H^6\left(\frac{e_1}{t_1} - \frac{e}{t}\right) = (\sqrt{t_1}-G)^6 - (\sqrt{t}-G)^6 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

From the second and third, we have

$$H^6\left(\frac{e}{t} - \frac{e_0}{t_0}\right) = (\sqrt{t}-G)^6 - (\sqrt{t_0}-G)^6 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

Dividing (3) by (4), we obtain a known ratio R,

$$R = \frac{\frac{e_1}{t_1} - \frac{e}{t}}{\frac{e}{t} - \frac{e_0}{t}} = \frac{(\sqrt{t_1}-G)^6 - (\sqrt{t}-G)^6}{(\sqrt{t}-G)^6 - (\sqrt{t_0}-G)^6} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

From this we may eliminate G by trial and error. The shortest way of making this computation is, perhaps, the following :—

Assume any value A for G, and substitute it in (5), and compute the corresponding value of R, which let us denote by N. If we make the proportion, as the differential of N is to the differential of A, so is the difference between N and R to δ, the difference between A and G, we have

$$\tfrac{1}{6} \times \frac{\{(\sqrt{t_1} - A)^6 - (\sqrt{t} - A)^6\} - \{(\sqrt{t} - A)^6 - (\sqrt{t_0} - A)^6\}\,R}{\{(\sqrt{t} - A)^5 - (\sqrt{t_0} - A)^5\}\,N - \{(\sqrt{t_1} - A)^5 - (\sqrt{t} - A)^5\}} = \delta, \text{ and } A - \delta = A_1,$$

which approximates nearer to G. Substituting this value in the place of A in the above equation, we obtain the next value of δ, which call δ_1, and $A_1 - \delta_1 = A_2$, which approximates still nearer to G.

We arrive more quickly at the exact value of G by making $A - \frac{N}{R}\delta = A_1$, and $A_1 - \frac{N_1}{R}\delta_1 = A_2$. Having thus found A_1, A_2, N, N_1, N_2, we may lay off A as the ordinate to N, A_1 to N_1, and A_2 to N_2, then, drawing a curve through these points, the ordinate to it opposite R is G, which, in this way, may be obtained very exactly.

As an example the following three observations are taken from Professor MAGNUS's experiments on the elastic force of steam, that have recently appeared in the 14th number of the 'Scientific Memoirs.'

$e_0 = 0{\cdot}178$	$t_0 = 493 = (461 + 32)$
$e = 3{\cdot}793$	$t = 585{\cdot}1 = (461 + 124{\cdot}1)$
$e_1 = 29{\cdot}920$	$t_1 = 673 = (461 + 212)$

Computing the preceding formulæ with these data, a few trials give G = 19·625. Then, by (3) or (4), we get H = 10·62, and by (2), from the first experiment at the lowest temperature, we obtain the value of F^6, and thence $F^6(51 + 461) = 0{\cdot}08$, or $\frac{1}{375}$th part of an atmosphere of permanently elastic matter at 51° Fahr.

The line on the chart which answers to the experiments of SOUTHERN and the French Academy has G = 19·492, and H = 10·83.

It is obvious that one of the experiments ought to be taken at as low a temperature as possible, and that F^6 should be computed from its data.

The general formula for vapour, $t\left(\frac{\sqrt{t} - G}{H}\right)^6 = e$, is easy to compute when the tension for a given temperature is required; but when the temperature that corresponds to a given tension is sought, the equation does not admit of direct solution. The following is, perhaps, the simplest method of overcoming the difficulty. It is founded on the property of the tangent to the curve of constant pressure, alluded to in Note B.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

The length of that portion of it intercepted between the point of contact and the axis of the curve, is equal to three times the length of the abscissa.

The tension given being ϵ, and the corresponding absolute temperature τ being required, assume any absolute temperature as near to τ as may be guessed roughly; then, by the formula for the given vapour, $t\left(\frac{\sqrt{t}-\mathrm{G}}{\mathrm{H}}\right)^6 = e$, compute e. The value of τ may then be found directly, with all necessary precision, by the following equation:

$$\tau = \left\{\frac{4\mathrm{H}\sqrt[6]{\epsilon} + 3\mathrm{G}\sqrt[6]{t}}{\frac{\mathrm{H}}{\sqrt{t}}\sqrt[6]{\epsilon} + 3\sqrt[6]{t}}\right\}^2.$$

From this value of τ subtract 461, and we have the temperature required on Fahr. scale that corresponds to the elastic force ϵ.

J. J. WATERSTON.

December 15, 1845.

EXPLANATION OF TABLE OF GASES AND VAPOURS.

Received February 19, 1846.

Having found the following Table useful to refer to while studying the subject of gases and vapours, I have been led to hope that it might be made available, so far as it goes, in shortening the labour of drawing up a complete view of their physical constants. That such a condensed view of their physical character and constitution is a desideratum will probably be generally admitted, and principally with reference to theoretical chemistry does it seem to be of importance to have their molecular characteristics placed before the eye in a clear and concise manner.

The tables of this description that are usually inserted in chemical treatises do not, perhaps, give to the arithmetic of volumes all the clearness that it is susceptible of. This is a consequence of employing the chemical equivalent or lowest combining proportion as the unit, whether or not it happens to correspond with the specific gravity of the gas, and it is generally either half this ratio or, as in the case of sulphur, of phosphorus, and of arsenic, even a smaller fraction of it.

Thus we have H + O the symbol for water. In Dr. TURNER'S 'Chemistry' its constitution is thus defined: 1, or one equivalent of hydrogen, + 8, or one equivalent of oxygen, = 9 the equivalent of water; and, by volume, 100 of hydrogen combines with 50 of oxygen to form 100 of steam. If we take 16 as the equivalent of oxygen, which corresponds with its specific gravity, then $\mathrm{HO}_{\frac{1}{2}}$ expresses distinctly the constitution of steam both by weight and volume. Another objectionable point may sometimes be remarked though it has now almost disappeared, the combining ratio by volume is inserted before any determination of the fact has been made: thus

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

Dr. TURNER defines the peroxide of hydrogen, 100 volumes, to consist of 100 oxygen + 100 hydrogen, whereas, since the vapour has never been weighed, it is just as likely to consist of 50 volumes of each; both gases unite with others in several instances in half volumes, so that, until the experiment has been made, all that can be stated is that 17 by weight of the peroxide consists of 1 hydrogen + 16 oxygen. As soon as we have ascertained the space occupied by the 17 of the peroxide in comparison to the 1 of the hydrogen we can state its composition by volume, but it is surely confusing the subject of volumes altogether to infer this from the combining weights alone.

In this Table the specific gravity of a simple gas in terms of hydrogen unity is taken as the value of its symbol (Col. 3, Part I.), and when this is inserted in parentheses (as from Nos. 10 to 20), it represents the value that has been assigned to the symbolical letter of the element in the compounds that follow, and indicates that it has not as yet been weighed in the simple vapour.

Thus the value of C is 12, of F 19, &c., throughout the Table wherever these letters occur, and at the side these numbers are taken as unity in denoting the several proportions with which they have been found to combine in a single volume of compound gases and vapours. Opposite hydrogen, for example, we see numbers from $\frac{1}{2}$ up to 16, which informs us that from $\frac{1}{2}$ a volume up to 16 volumes of this gas enters into one volume of its compounds, and the same with regard to the others. These indicate in some degree the molecular capabilities of the element. They are ratios that have been taken from vapours that have actually been weighed as well as analysed. A large proportion of them are of recent determination, and the original details of the experiments by DUMAS, MITSCHERLICH, REGNAULT, LAURENT, and BINEAU are to be found for the most part in the 'Annales de Chimie'; the reference to the volume and page of this invaluable work is given in parentheses after the name of the vapour, and the letter (m) is a reference to MITSCHERLICH'S 'Chemistry,' where several specific gravities of vapour are given that are not to be found elsewhere.

In the table of binary compounds a column is occupied with the chemical constitution of a single volume of each in terms of volumes of its elementary components. Thus, nitric acid is represented by $O_{2\frac{1}{2}}N$, which means that one volume of nitric acid vapour is composed of $2\frac{1}{2}$ volumes oxygen united to one volume nitrogen, and where a volume has not been weighed, although its constitution by weight is known, the symbol is within parentheses, thus [ ].

In the ternary and organic compounds the simple constitution of a volume is given in the first place, as with the binary, and in the next column the most probable arrangement of the constituents, when there is any ground for making a hypothesis.

Thus we have oxalic ether, No. 114, evidently composed of one volume oxalic acid and one volume of sulphuric ether condensed into one volume. This also allows us to infer with great probability the specific gravity of oxalic acid vapour. The next is nitrous ether, No. 115, which is quite a similar compound in the liquid form, but it

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

will be remarked that in the act of rising into vapour it is decomposed, and what is one volume in the case of oxalic ether vapour is two volumes in the case of nitrous ether. Several other examples of this kind will be found. I have already referred to such facts as being favourable to the hypothesis of media which attributes a mechanical origin to the law of volumes, and have likewise referred to the remarkable circumstance that compounds which thus disunite in the act of vaporization nevertheless obey the general law of vapours (see Note B). As it seems, from the nature of the function that expresses this law, that a mechanical origin may be found for it also, the investigation of the subject might, perhaps, be made easier if the chart lines of vapour were determined for mixtures of pure alcohol and water in all proportions, and also for mixtures of alcohol and ether.

We should then, perhaps, discover the law of variation of the two constants G and H of the chart line, and this might provide us with a new condition or effect of the primary cause pointing to its origin from a new ground.

The two last columns contain the constants G and H, referred to in Note B.; where there are three places of decimals the numbers are nearly exact, when two only they are to be considered as approximate.

Column No. 1 contains the temperature on Fahrenheit scale at which the vapour in contact with its generating solid or liquid equilibrates a pressure of 30 inches of mercury.

Column No. 2 contains the specific gravity of the body in its usual liquid or solid form.

Column No. 3 contains, as before mentioned, the specific gravity of the body in its gaseous form in terms of hydrogen unity. It expresses the weight of a molecule of the hypothetical medium that answers to the gas in its physical relations.

Column No. 4 contains the inverse of the specific heat of the body in its usual liquid, solid, or gaseous form. The numbers are found by dividing the constant 3·2 by the specific heat. This constant is the product of the specific heat of air by its specific gravity in terms of hydrogen unity, and to the same product of all gases that conform to the law of equal volumes having the same specific heat. It is likewise the product of the specific heat of mercury in its liquid form by the specific gravity of its vapour (Note E). In other elementary bodies this product is a simple multiple of the same constant. In compounds the same product is also in most cases a simple multiple of the same constant. On the *vis viva* theory of heat the numbers in this column probably show the mean weight of the component parts of the gaseous molecule that have an independent motion when the body is in the liquid or solid form. Thus, No. 33, arsenious acid: the specific gravity of the vapour is 200 times that of hydrogen; but its specific heat in the solid form is 8 times what it is in the state of vapour, if in this form it obeyed the law of the specific heat of gases. Hence 25 is the number opposite in this column, which, since it goes 8 times in 200, shows that the molecule consists of about 8 parts, each of which has an independent

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

motion. We see further that O_3As expresses the constitution of one volume of this acid, and referring to As, No. 7, we find that its specific heat in the solid form is nearly 4 times greater than it ought to be in the vapour.

The probable general inference is that such molecules consist of several parts, more or less free to move independently of each other, and that when they escape from the bonds of liquid cohesion and become free projectiles, these parts can no longer assume *vis viva* of their own, but are in subjection to the impressed condition of their common centre of gravity.

The great question in this department is, Do such compound bodies which have so great a specific heat in the solid form have it all at once reduced in so vast a proportion when raised to vapour? This interesting point, as remarked at length in Note B, has yet to be determined by an experiment made on the specific heat of sulphuric ether vapour, as being the most accessible, which, if these views are correct, ought to be only about $\frac{1}{6}$th of the specific heat of the liquid.

Column No. 5 contains the quotient of the gaseous specific gravity by the specific gravity of the liquid or solid, and represents the relative size of the molecules. The subject of atomic volume has recently been the subject of interesting discussion by M. Kopp ('Ann. de Chim.,' vol. 75, 1840, p. 406), and, doubtless, will increase in importance as science advances.

To these physical characteristics of gases it would be well if we could add the temperature of liquefaction, the latent heat of liquefaction, or the measure of the solid polar cohesion of molecules according to the *vis viva* theory, the differential of expansion through a range of temperature, and the latent heat of vapours or measure of liquid molecular cohesion.

December 24, 1845. J. J. Waterston.

This paper being the last in connection with the *vis viva* theory of gases that the writer is likely to have an opportunity of submitting to the Society, he begs, in taking leave of the subject, to express a hope that, although the nature of the fundamental hypothesis is likely to be repulsive to mathematicians, they will not reject it without a fair trial. The principle of the conservation of *vis viva* involves the indestructibility of force, and is a necessary consequence of the quality of perfect elasticity or reaction in the ultimate elements of matter: if this last is a universal property the first must also be of universal effect, and, as it does not admit of any diminution of force in nature, we may question whether, in such intense chemical action as the phenomena of combustion and explosion manifest, the sudden evolution of force is not merely an exhibition of its transference from one form of elastic matter to another.

Are not the properties of aeriform fluids and of the medium of light glaring proofs of the widely spread existence of this quality of perfect elasticity, whatever may be

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

its essential mode of reaction; and do not they even demand of us a ready assent to its all-prevailing influence in the phenomena of Nature?

Although the utmost caution in adopting any hypothesis is the proper accompaniment of a sober spirit of inquiry, it does not appear inconsistent with such a spirit to advocate the trial of these principles as a foundation for mathematical research in the several departments of molecular physics.

It is the matured conviction of the writer that upon such foundation we shall have to build if we are destined ever to become acquainted with the secret mechanism of Nature. Would that his feeble voice could call attention to the subject, could direct upon it some portion of the vast mathematical talent that this country can now, more than at any former period, boast of.

J. J. W.

TABLE OF GASES AND VAPOURS.—I. Elementary Substances.

		Symbol.	Chemical equivalent.	Boiling temperature.	Specific gravity.	Gaseous specific gravity. H = 1.	Ditto inferred from specific heat.	Bulk of a molecule.	Combining proportions in volumes.	Vapour constants.*	
				1.	2.	3.	4.	5.		G.	H.
1	Oxygen	O	8	° ..	..	16	16	..	$\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, ($3\frac{1}{2}$?)		
2	Hydrogen	H	1	..	..	1	1	..	$\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, 3, 4, 5, 6, 8, 9, 16		
3	Nitrogen	N	14·1	..	..	14	14	..	$\frac{1}{2}$, 1		
4	Chlorine	Cl	35·4	6	1·33	36	..	27	$\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$	17·0	7·24
5	Bromine (55/31)	Br	78·4	116	3·00	80	24	27	$\frac{1}{2}$, 1, $1\frac{1}{2}$		
6	Iodine	I	126·3	350	4·95	125	{35, 39, 60}	25	$\frac{1}{2}$, 1, $1\frac{1}{2}$		
7	Arsenic (55/32)	As	37·7	356	5·88	152	40	26	$\frac{1}{4}$, 1		
8	Sulphur (50/170; 55/31)	S	16·1	600	1·99	96	16	48	$\frac{1}{6}$, $\frac{2}{6}$		
9	Phosphorus (49/211; 50/170)	P	15·7	500	1·71	64	{16, 8}	38	$\frac{1}{4}$		
10	Mercury (55/32)	Hg	202	650	13·57	101	101	7·3	1	22·606	20·002
11	Fluorine	F	18·7	..	(0·73 ?)	[19]	..	..	$\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$		
12	Carbon	C	6·1	..	{3·52, 2·50}	[12]	{26, 12, 19}	3·4	$\frac{1}{2}$, 1, 2, 3, $3\frac{1}{2}$, 4, $4\frac{1}{2}$, 5, $7\frac{1}{2}$, 8, 10		
13	Boron	B	10·9	..	{1·18, 1·84}	[11]	..	..	$\frac{1}{2}$		
14	Silicon	Si	7·5	..	..	[15]	..	..	1		
15	Selenium	Se	39·6	650	4·31	[40]	40	9·2	1		
16	Tin	Sn	58·9	..	7·29	[58]	58	8	1		
17	Antimony	Sb	64·6	..	6·70	[64]	64	9·5	1		
18	Titanium	Ti	24·3	..	5·30	[24]	..	4·5	1		
19	Tellurium	Te	32·3	..	6·11	[64]	64	10·5	1		
20	Chromium	Cr	28·0	..	5·90	[28]	..	5·5	1		

* See note B.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

II. Binary Compounds.

		Boiling temperature.	Specific gravity.	Gaseous specific gravity. H = 1.	Ditto inferred from specific heat.	Bulk of a molecule.	Chemical analysis.	Chemical arrangement of molecules (hypothesis).	Vapour constants.	
		1.	2.	3.	4.	5.			G.	H.
21	Water	212°	1·00	9	3·2	9·0	$O_{\frac{1}{2}}H$		19·492	10·830
22	Peroxide of hydrogen	..	1·45	[$8\frac{1}{2}$]	..	[6·0]	[$O_{\frac{1}{2}}H_{\frac{1}{2}}$]			
23	Binoxide of nitrogen	..	..	15	..	..	$O_{\frac{1}{2}}N_{\frac{1}{2}}$			
24	Nitrous oxide	..	..	22	..	..	$O_{\frac{1}{2}}N$			
25	Nitrous acid	82	1·45	46	..	32	O_2N			
26	Hyponitrous acid (55/32)	[0 ?]	[1·1 ?]	25·3	..	..	$ON_{\frac{2}{3}}$	$2(O_{\frac{1}{2}}N_{\frac{1}{2}}) + O_2N = 3$ vols.		
27	Nitric acid	..	1·70	54	..	32	$O_{2\frac{1}{2}}N$			
28	Quadrihydrate of nitric acid (68/417)	248	1·42	18	..	63	$O_{\frac{8}{10}}N_{\frac{1}{5}}H_{\frac{4}{5}}$	$O_{2\frac{1}{2}}N + 4(HO_{\frac{1}{2}}) = 5$ vols.		
29	Carbonic oxide	..	..	14	..	..	$O_{\frac{1}{2}}C_{\frac{1}{2}}$			
30	Carbonic acid	[−160 ?]	{·83 ·45}	22	22	..	$OC_{\frac{1}{2}}$		10·09	10·62
31	Oxalic acid	[330]	[2·4 ?]	[36]	..	..	[$O_{1\frac{1}{2}}C$]			
32	Oxalic hydrate	..	..	[45]	..	..	[O_2HC]			
33	Arsenious acid (55/35)	380	3·7	200	25	54	O_3As			
34	Arsenic acid	..	[4·3 ?]	[232]	..	[54 ?]	[O_5As]			
35	Sulphurous acid	14	1·42	32	..	..	$OS_{\frac{1}{6}}$		17·38	6·97
36	Sulphuric acid (55/32)	115	2·29	40	9·2	17	$O_{1\frac{1}{2}}S_{\frac{1}{6}}$			
37	Sulphuric hydrate	620	1·85	[49]	..	[27]				
38	Ammonia	− 46 ?	0·76	$8\frac{1}{2}$	..	11·3	$H_{1\frac{1}{2}}N_{\frac{1}{2}}$		13·40	10·80
39	Arseniuretted hydrogen	..	..	$39\frac{1}{2}$	..	..	$H_{1\frac{1}{2}}As_{\frac{1}{2}}$			
40	Selenious acid (55/36)	..	..	56	..	..	SeO			
41	Sulphuretted hydrogen	− 90 ?	0·90	17	..	$18\frac{1}{2}$	$HS_{\frac{1}{6}}$			

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

II. Binary Compounds (continued).

		Boiling temperature.	Specific gravity.	Gaseous specific gravity. H = 1.	Ditto inferred from specific heat.	Bulk of a molecule.	Chemical analysis.	Chemical arrangement of molecules (hypothesis).	Vapour constants.	
		1.	2.	3.	4.	5.			G.	H.
42	Bisulphuretted hydrogen	..	1·77	[$16\frac{1}{2}$]	..	..	[$H_{\frac{1}{2}}S_{\frac{1}{6}}$]			
43	Phosphoretted hydrogen	..	..	$17\frac{1}{2}$	..	..	$H_{1\frac{1}{2}}P_{\frac{1}{4}}$			
44	Seleniuretted hydrogen (68/423)	..	..	41	..	..	HSe			
45	Tellurated hydrogen	..	..	65	..	..	HTe			
48	Muriatic acid	− 160 ?	2·30 ?	$18\frac{1}{2}$	..	[8]	$H_{\frac{1}{2}}Cl_{\frac{1}{2}}$			
49	Octohydrate of muriatic acid (68/423)	..	1·16	$10\frac{1}{18}$	..	..	$H_{\frac{17}{18}}Cl_{\frac{1}{18}}O_{\frac{4}{9}}$	$Cl_{\frac{1}{2}}H_{\frac{1}{2}} + 8(HO_{\frac{1}{2}}) = 9$ vols.		
50	Hydrobromic acid (55/9)	..	1·76	$40\frac{1}{2}$	..	23	$H_{\frac{1}{2}}Br_{\frac{1}{2}}$			
51	Hydroiodic acid	..	..	63	..	..	$H_{\frac{1}{2}}I_{\frac{1}{2}}$			
52	Hydrofluoric acid	60	1·06	[10]	..	[9]	$H_{\frac{1}{2}}F_{\frac{1}{2}}$			
53	Cyanogen	− 8	0·90	26	..	29	NC	. . . . .	17·08	6·55
54	Bisulphuret of mercury (55/36)	..	..	80	..	..	$S_{\frac{1}{9}}M_{\frac{2}{3}}$	$S_{\frac{1}{6}}M + S_{\frac{1}{6}} + M = 3$ vols. ?		
55	Sulphuret of carbon	117·2	1·27	38	10	31	$S_{\frac{1}{3}}C_{\frac{1}{2}}$	. . . . .	16·254	12·760
56	Protoxide of chlorine (euchlorine) (m)	..	..	35·2	..	..	$O_{\frac{2}{5}}Cl_{\frac{4}{5}}$	$[OCl_{\frac{1}{2}} + Cl] = 2$ vols. ?		
57	Peroxide of chlorine (m)	..	..	34·0	..	..	$OCl_{\frac{1}{2}}$			
58	Perchloric acid	392	1·65	[92]	..	..	[$O_{3\frac{1}{2}}Cl$]			
59	Quadrichloride of nitrogen	160	1·65	[79]	..	..	[$Cl_2N_{\frac{1}{2}}$]			
60	Sesquichloride of arsenic	..	..	92	..	..	$Cl_{1\frac{1}{2}}As_{\frac{1}{4}}$			
61	Sesquibromide of arsenic	..	..	158	..	..	$Br_{1\frac{1}{2}}As_{\frac{1}{4}}$			
62	Periodide of arsenic (55/35)	..	..	225	..	..	$I_{1\frac{1}{2}}As_{\frac{1}{4}}$			
63	Chloride of sulphur	147	1·62	52	..	32	$ClS_{\frac{1}{6}}$			
64	Dichloride of sulphur	280	1·69	68	..	40	$ClS_{\frac{2}{6}}$			

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

II. Binary Compounds (continued).

		Boiling temperature.	Specific gravity.	Gaseous specific gravity. H = 1.	Ditto inferred from specific heat.	Bulk of a molecule.	Chemical analysis.	Chemical arrangement of molecules (hypothesis).	Vapour constants.	
		1.	2.	3.	4.	5.			G.	H.
65	Sesquichloride of phosphorus (m)	205°	1·45	70	..	48	$Cl_{1\frac{1}{2}}P_{\frac{1}{4}}$			
66	Perchloride of phosphorus (m; 55/5)	180	..	71	..	..	$Cl_{\frac{5}{3}}P_{\frac{1}{6}}$	$Cl_{2\frac{1}{3}}P_{\frac{1}{4}} + Cl + Cl_{1\frac{1}{12}}P_{\frac{1}{4}} = 3$ vols.?		
67	Protochloride of mercury	..	7·14	118	..	16	$Cl_{\frac{1}{2}}Hg$			
68	Bichloride of mercury	..	5·42	136	..	26	$ClHg$			
69	Protobromide of mercury	..	7·31	140	..	19	$Br_{\frac{1}{2}}Hg$			
70	Bibromide of mercury	..	5·92	180	..	30	$BrHg$			
71	Biniodide of mercury	..	..	227	..	..	IHg			
72	Dichloride of carbon	400	..	[144]	..	..	$[Cl_3C_3]$			
73	Protochloride of carbon (71/374)	252	1·62	84	..	52	Cl_2C			
74	Perchloride of carbon	360	2·00	[120]	..	..	$[Cl_3C]$			
75	Perchloride of muriate of methyle (71/385)	173	1·60	78	..	49	$Cl_2C_{\frac{1}{2}}$			
76	Terchloride of boron (55/14)	..	..	$59\frac{1}{2}$	..	..	$Cl_{1\frac{1}{2}}B_{\frac{1}{2}}$			
77	Fluoride of boron	..	..	33	..	..	$F_{1\frac{1}{2}}B_{\frac{1}{2}}$			
78	Chloride of silicium	124	..	87	..	..	Cl_2Si			
79	Fluoride of silicium	..	..	62	..	..	$Fl_{2\frac{1}{2}}Si$			
80	Bichloride of tin	..	..	130	..	..	Cl_2Sn			
81	Sesquichloride of antimony (55/36)	..	..	118	..	..	$Cl_{1\frac{1}{2}}Sb$			
82	Bichloride of titanium (55/13)	220	..	96	..	..	Cl_2Ti			

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

III. Ternary, &c., Compounds.

		Boiling temperature.	Specific gravity.	Gaseous specific gravity. H = 1.	Ditto inferred from specific heat.	Bulk of a molecule.	Chemical analysis.	Chemical arrangement of molecules (hypothesis).	Vapour constants.	
		1.	2.	3.	4.	5.			G.	H.
83	Hydrocyanic gas	80°	0·70	$13\frac{1}{2}$	..	19	$H_{\frac{1}{2}}N_{\frac{1}{2}}C_{\frac{1}{2}}$	$H_{\frac{1}{2}} + \frac{1}{2}(NC)$		
84	Chloride of cyanogen	12	1·32	31	..	$23\frac{1}{2}$	$Cl_{\frac{1}{2}}N_{\frac{1}{2}}C_{\frac{1}{2}}$	$Cl_{\frac{1}{2}} + \frac{1}{2}(NC)$	16·43	8·42
85	Terchloride of cyanogen (68/424)	374	4·0 ?	93	..	23 ?	$Cl_{1\frac{1}{2}}N_{1\frac{1}{2}}C_{1\frac{1}{2}}$	$3(Cl_{\frac{1}{2}} + \frac{1}{2}(NC))$		
86	Bromide of cyanogen	100	2·2 ?	53	..	23 ?	$Br_{\frac{1}{2}}N_{\frac{1}{2}}C_{\frac{1}{2}}$	$Br_{\frac{1}{2}} + \frac{1}{2}(NC)$		
87	Chlorocarbonic oxide gas	..	..	50	..	..	$ClO_{\frac{1}{2}}C_{\frac{1}{2}}$	$Cl + O_{\frac{1}{2}}C_{\frac{1}{2}}$		
88	Oxichloride of chromium	..	..	80	..	..	ClOCr	Cl + OCr		
89	Chlorosulphuric acid (71/445)	170	1·66	68	..	41	$ClOS_{\frac{1}{6}}$	$Cl + OS_{\frac{1}{6}}$		
90	Anhydrous carbonate of ammonia (68/434)	..	..	13	..	..	$O_{\frac{1}{3}}C_{\frac{1}{6}}N_{\frac{1}{3}}H$	$OC_{\frac{1}{2}} + 2(N_{\frac{1}{2}}H_{1\frac{1}{2}}) = 3$ vols.		
91	Anhydrous hydrosulphate of ammonia	180	..	$12\frac{3}{4}$	..	..	$S_{\frac{1}{12}}N_{\frac{1}{4}}H_{1\frac{1}{4}}$	$S_{\frac{1}{6}}H + N_{\frac{1}{2}}H_{1\frac{1}{2}} = 2$ vols.		
92	Anhydrous hydrocyanate of ammonia	..	..	11	..	..	$N_{\frac{1}{2}}C_{\frac{1}{4}}H$	$H_{\frac{1}{2}}N_{\frac{1}{2}}C_{\frac{1}{2}} + N_{\frac{1}{2}}H_{1\frac{1}{2}} = 2$ vols.		
93	Anhydrous hydrotellurate of ammonia	174	..	$36\frac{3}{4}$	..	..	$N_{\frac{1}{4}}Te_{\frac{1}{2}}H_{1\frac{1}{4}}$	$HTe + N_{\frac{1}{2}}H_{1\frac{1}{2}} = 2$ vols.		
94	Anhydrous muriate of ammonia (sal. am.)	..	..	$13\frac{1}{2}$	..	..	$Cl_{\frac{1}{4}}HN_{\frac{1}{4}}$	$Cl_{\frac{1}{2}}H_{\frac{1}{2}} + N_{\frac{1}{2}}H_{1\frac{1}{2}} = 2$ vols.		
95	Hydroiodate of phosphoretted hydrogen	174	..	..	..	..	$I_{\frac{1}{4}}HP_{\frac{1}{8}}$	$I_{\frac{1}{2}}H_{\frac{1}{2}} + P_{\frac{1}{4}}H_{1\frac{1}{2}} = 2$ vols.		
96	Hydrobromate of phosphoretted hydrogen	85	..	..	..	..	$Br_{\frac{1}{4}}HP_{\frac{1}{8}}$	$Br_{\frac{1}{2}}H_{\frac{1}{2}} + P_{\frac{1}{4}}H_{1\frac{1}{2}} = 2$ vols.		
97	Hydrochlorate of phosphoretted hydrogen	..	..	18	..	..	$Cl_{\frac{1}{4}}HP_{\frac{1}{8}}$	$Cl_{\frac{1}{2}}H_{\frac{1}{2}} + P_{\frac{1}{4}}H_{1\frac{1}{2}} = 2$ vols.		

IV. Organic Compounds.

		Boiling temperature.	Specific gravity.	Gaseous specific gravity. H = 1.	Ditto inferred from specific heat.	Bulk of a molecule.	Chemical analysis.	Chemical arrangement of molecules (hypothesis).	Vapour constants.	
		1.	2.	3.	4.	5.			G.	H.
98	Carburetted hydrogen	° ..	..	8	..	..	$H_2C_{\frac{1}{2}}$			
99	Olefiant gas or etherin or hydrocarbon	..	(0·63) ?	14	14	(22 ?)	H_2C	$\frac{1}{2}$, 1, 2, $4\frac{1}{2}$, 5, 8 (combining ratios)		
100	Etherine or bietherin	0	0·63	28	6·7	(45)	H_4C_2	$2\,(H_2C) = (H_2C)_2$		
101	Elaen	230	..	63	..	..	$H_9C_{4\frac{1}{2}}$	$4\frac{1}{2}\,(H_2C) = (H_2C)_{4\frac{1}{2}}$		
102	Ameline	320	0·85	70	..	82	$H_{10}C_5$	$5\,(H_2C) = (H_2C)_5$		
103	Ceten	527	..	112	..	..	$H_{16}C_8$	$8\,(H_2C) = (H_2C)_8$		
104	Benzin or bicarburet of hydrogen (55/45)	187	0·85	39	..	44	H_3C_3			
105	Mesitylene (70/103)	330	..	40	..	..	H_4C_3			
106	Naphtha	180	0·75	41	6·5	56	H_5C_3	. . . . .	19·36	14·64
107	Naphthalin (50/183)	412	..	64	..	..	H_4C_5			
108	Paranaphthalin	572	..	96	..	..	H_6C_5			
109	Camphene or oil of turpentine (75/41)	332	0·86	68	6·6	80	H_8C_5	. . . . .	18·59	15·56
110	Caoutchin or citrene (70/103)	440	0·67	68	..	102	H_8C_5			
111	Petrolene or sweet oil of wine (71/411)	545	0·90	136	..	151	$H_{16}C_{10}$			
112	Alcohol	173	·795	23	5·0	29	$H_3CO_{\frac{1}{2}}$	$H_2C + HO_{\frac{1}{2}}$	19·20	10·00
113	Sulphuric ether	96	{·734 ·632}	37	5·8	58	$H_5C_2O_{\frac{1}{2}}$	$(H_2C)_2 + HO_{\frac{1}{2}}$	16·86	10·99
114	Oxalic ether (m)	400	1·09	73	..	66	$H_5C_3O_2$	$O_{1\frac{1}{2}}C + (H_2C)_2 + HO_{\frac{1}{2}}$		
115	Nitrous ether (m)	80	·89	$37\frac{1}{2}$	..	42	$H_{2\frac{1}{2}}ON_{\frac{1}{2}}C$	$\overline{O_{1\frac{1}{2}}N} + \overline{(H_2C)_2 + HO_{\frac{1}{2}}} = 2$ vols.		
116	Succinic ether (m)	515	1·04	87	..	84	$H_7C_4O_2$	$O_{1\frac{1}{2}}H_2C_2 + (H_2C)_2 + HO_{\frac{1}{2}}$		

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

IV. Organic Compounds (continued).

		Boiling temperature.	Specific gravity.	Gaseous specific gravity. H = 1.	Ditto inferred from specific heat.	Bulk of a molecule.	Chemical analysis.	Chemical arrangement of molecules (hypothesis).	Vapour constants.	
		1.	2.	3.	4.	5.			G.	H.
117	Formic ether (m)	132°	·92	37	..	80	$H_3C_{1\frac{1}{2}}O$	$\overline{O_{1\frac{1}{2}}HC} + \overline{(H_2C)_2 + HO_{\frac{1}{2}}} = 2$ vols.		
118	Acetic ether (m) (see 132 and 139) . .	205	·89	44	..	100	H_4C_2O	$\overline{O_{1\frac{1}{2}}H_3C_2} + \overline{(H_2C)_2 + HO_{\frac{1}{2}}} = 2$ vols.		
119	Mercaptan or hydrosulph. of etherine (71/391)	{96, 143}	·83	31	..	38	$H_3CS_{\frac{1}{6}}$	$H_2C + HS_{\frac{1}{6}}$		
120	Hydrosulphuric ether or hydrosulph. of etherine (71/389)	160	·825	45	..	55	$H_5C_2S_{\frac{1}{6}}$	$(H_2C)_2 + HS_{\frac{1}{6}}$		
121	Benzoic acid or anhydrous carbonate of benzin (55/46)	528	·66	61	..	92	$H_3C_{3\frac{1}{2}}O$	$H_3C_3 + OC_{\frac{1}{2}}$		
122	Nitrobenzide or nitrite of benzin (57/87)	400	1·21	62	..	51	$H_3C_3ON_{\frac{1}{2}}$	$H_3C_3 + ON_{\frac{1}{2}}$		
123	Oxidized ether or aldehyde (m) (59/295)	72	·79	22	..	28	$H_2CO_{\frac{1}{2}}$	$(H_3C_3)_{\frac{1}{3}} + HO_{\frac{1}{2}}$ or $H_2C + O_{\frac{1}{2}}$		
124	Chloric ether (m)	220	1·07	32	..	30	$H_2CCl_{\frac{1}{2}}$	$H_2C + Cl_{\frac{1}{2}}$		
125	Chloride of hydrocarbon (58/307) . .	{178, 146}	{1·26, 1·17}	50	..	40	H_2CCl	$H_2C + Cl$		
126	Bromide of hydrocarbon (59/359) . .	322	2·16	94	..	43	H_2CBr	$H_2C + Br$		
127	Iodide of hydrocarbon	..	3·20	..	..	..	$[H_2CI]$			
128	Hydrochloric ether (Thenard) . . .	57	{0·84, 0·77}	$32\frac{1}{2}$	..	40	$H_{2\frac{1}{2}}Cl_{\frac{1}{2}}C$	$H_2C + Cl_{\frac{1}{2}}H_{\frac{1}{2}}$		
129	Hydrobromic ether	..	..	$[54\frac{1}{2}]$	..	..	$H_{2\frac{1}{2}}Br_{\frac{1}{2}}C$	$H_2C + Br_{\frac{1}{2}}H_{\frac{1}{2}}$		
130	Hydroiodic ether (Gay-Lussac and Thenard)	{176, 148}	1·92	77	..	40	$H_{2\frac{1}{2}}I_{\frac{1}{2}}C$	$H_2C + I_{\frac{1}{2}}H_{\frac{1}{2}}$		
131	Hydrocyanic ether	216	0·79	$27\frac{1}{2}$	..	35	$H_{2\frac{1}{2}}N_{\frac{1}{2}}C_{1\frac{1}{2}}$	$H_2C + N_{\frac{1}{2}}C_{\frac{1}{2}}H_{\frac{1}{2}}$		
132	Acetic ether (49/209). Pyroacetic spirit (see 118 and 139)	132	0·79	29	..	37	$H_3C_{1\frac{1}{2}}O_{\frac{1}{2}}$	$H_2C + O_{\frac{1}{2}}C_{\frac{1}{2}}H$		

IV. Organic Compounds (continued).

		Boiling temperature.	Specific gravity.	Gaseous specific gravity. H = 1.	Ditto inferred from specific heat.	Bulk of a molecule.	Chemical analysis.	Chemical arrangement of molecules (hypothesis).	Vapour constants.	
		1.	2.	3.	4.	5.			G.	H.
133	Methylal (70/394)	107°	0·85	38	..	44	$H_4C_{1\frac{1}{2}}O$	$(H_2C+O_{\frac{1}{2}}C_{\frac{1}{2}}H)+HO_{\frac{1}{2}}$		
134	Benzoic ether (m)	502	1·05	75	..	71	$H_5C_{4\frac{1}{3}}O$	$H_2C+(H_3C_3+C_{\frac{1}{3}}O)$		
135	Pyroxilic spirit (58/11)	150	·80	16	..	20	$H_2C_{\frac{1}{2}}O_{\frac{1}{2}}$	$(H_2C)_{\frac{1}{2}}+HO_{\frac{1}{2}}$ . .	18·06	11·00
136	Pyroxilic ether (58/21)	..	·80	23	..	29	$H_3CO_{\frac{1}{2}}$	$H_2C+HO_{\frac{1}{2}}$		
137	Nitrate of pyroxilic ether (58/42)	156	1·18	$38\frac{1}{2}$	..	65	$H_{1\frac{1}{2}}C_{\frac{1}{2}}O_{1\frac{1}{2}}N_{\frac{1}{2}}$	$\overline{O_{2\frac{1}{2}}N}+\overline{H_2C+HO_{\frac{1}{2}}}=2$ vols.		
138	Sulphate of pyroxilic ether (58/34)	370	1·32	63	..	48	$H_3CO_2S_{\frac{1}{6}}$	$\overline{O_{1\frac{1}{2}}S_{\frac{1}{5}}}+\overline{H_2C+HO_{\frac{1}{2}}}=2$ vols.		
139	Acetate of pyroxilic ether (49/209; 58/47) (see 118 and 132)	136	·92	37	..	80	$H_3C_{1\frac{1}{2}}O$	$\overline{O_{1\frac{1}{2}}C_2H_3}+\overline{H_2C+HO_{\frac{1}{2}}}=2$ vols.		
140	Formicate of pyroxilic ether (m)	..	·80	30	..	38	H_2CO	$\overline{O_{1\frac{1}{2}}CH}+\overline{H_2C+HO_{\frac{1}{2}}}=2$ vols.		
141	Chloride of methyle (71/380)	85	1·34	43	..	32	$HClC_{\frac{1}{2}}$	$Cl+(H_2C)_{\frac{1}{2}}$		
142	Muriate of methyle (58/27)	..	[·82 ?]	$25\frac{1}{2}$	..	[32]	$H_{1\frac{1}{2}}Cl_{\frac{1}{2}}C_{\frac{1}{2}}$	$Cl_{\frac{1}{2}}H_{\frac{1}{2}}+(H_2C)_{\frac{1}{2}}$		
143	Hydroiodate of methyle (58/30)	110	2·24	70	..	31	$H_{1\frac{1}{2}}I_{\frac{1}{2}}C_{\frac{1}{2}}$	$I_{\frac{1}{2}}H_{\frac{1}{2}}+(H_2C)_{\frac{1}{2}}$		
144	Hydrofluorate of methyle (61/194)	..	..	17	..	..	$H_{1\frac{1}{2}}F_{\frac{1}{2}}C_{\frac{1}{2}}$	$F_{\frac{1}{2}}H_{\frac{1}{2}}+(H_2C)_{\frac{1}{2}}$		
145	Benzoate of methyle (58/52)	380	1·10	68	..	62	H_4C_4O	$(H_2C)_{\frac{1}{2}}+(H_3C_3+C_{\frac{1}{3}}O)$		
146	Formic acid (see 117 and 140 and 147)	..	1·16	[37]	..	[31]	$[HCO_{1\frac{1}{2}}]$			
147	Hydrate of formic acid (68/421)	..	1·12	23	..	20	$HC_{\frac{1}{2}}O$	$\overline{HCO_{1\frac{1}{2}}}+\overline{HO_{\frac{1}{2}}}=2$ vols.		
148	Hydrate of ameline (56/317)	265	0·82	44	..	54	$H_6C_{2\frac{1}{2}}O_{\frac{1}{2}}$	$(H_{10}C_5)_{\frac{1}{2}}+HO_{\frac{1}{2}}$		
149	Acetate of ameline (75/197)	257	..	65	..	..	$H_7C_{3\frac{1}{2}}O$	$H_2CO+(H_{10}C_5)_{\frac{1}{2}}$		
150	Hydroiodate of ameline (71/95)	248	..	98	..	..	$H_{5\frac{1}{2}}C_{2\frac{1}{2}}I_{\frac{1}{2}}$	$I_{\frac{1}{2}}H_{\frac{1}{2}}+(H_{10}C_5)_{\frac{1}{2}}$		
151	Camphor or oxide of camphene (m)	400	1·00	76	..	76	$H_8C_5O_{\frac{1}{2}}$	$H_8C_5+O_{\frac{1}{2}}$		

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

IV. Organic Compounds (continued).

		Boiling temperature.	Specific gravity.	Gaseous specific gravity. H = 1.	Ditto inferred from specific heat.	Bulk of a molecule.	Chemical analysis.	Chemical arrangement of molecules (hypothesis).	Vapour constants.	
		1.	2.	3.	4.	5.			G.	H.
152	Bichlorhydrate of camphene (75/37)	° ..	1·02	[86]	..	..	$H_{8\frac{1}{2}}C_5Cl_{\frac{1}{2}}$	$H_8C_5 + Cl_{\frac{1}{2}}H_{\frac{1}{2}}$		
153	Bromohydrate of camphene	..	1·28	[108½]	..	..	$H_{8\frac{1}{2}}C_5Br_{\frac{1}{2}}$	$H_8C_5 + Br_{\frac{1}{2}}H_{\frac{1}{2}}$		
154	Hydroiodate of camphene	..	1·51	[131]	..	..	$H_{8\frac{1}{2}}C_5I_{\frac{1}{2}}$	$H_8C_5 + I_{\frac{1}{2}}H_{\frac{1}{2}}$		
155	Valeric acid (m)	344	·94	81	..	86	H_5C_5O	$H_3C_3 + H_2C + 2(O_{\frac{1}{2}}C_{\frac{1}{2}})$		
156	Chloride of benzide (m) (see 160)	400	1·46	91½	..	62	$H_{1\frac{1}{2}}C_3Cl_{1\frac{1}{2}}$	$(H_{\frac{1}{2}}Cl_{\frac{1}{2}})_3C_3$		
157	Chloroetheride or chloroforme (71/382; 56/119)	141	1·48	60½	..	41	$H_{\frac{1}{2}}Cl_{1\frac{1}{2}}C_{\frac{1}{2}}$	$ClC_{\frac{1}{2}}(Cl_{\frac{1}{2}}H_{\frac{1}{2}})$		
158	Bromoetheride or bromoforme	..	3·1 ?	126½	..	[41]	$H_{\frac{1}{2}}Br_{1\frac{1}{2}}C_{\frac{1}{2}}$	$BrC_{\frac{1}{2}}(Cl_{\frac{1}{2}}H_{\frac{1}{2}})$*		
159	Iodetheride or iodiforme	255	5·0 ?	[194]	..	[41]	$[H_{\frac{1}{2}}I_{1\frac{1}{2}}C_{\frac{1}{2}}]$	$[IC_{\frac{1}{2}}(Cl_{\frac{1}{2}}H_{\frac{1}{2}})]$*		
160	Bichloride of muriatic ether (71/365) (see 156)	167	1·37	67½	..	50	$H_{1\frac{1}{2}}Cl_{1\frac{1}{2}}C$	$(H_{\frac{1}{2}}Cl_{\frac{1}{2}})_3C$		
161	Trichloride of muriatic ether	216	1·53	85	..	55	Cl_2HC	$Cl(H_{\frac{1}{2}}Cl_{\frac{1}{2}})_2C$		
162	Quadrichloride of muriatic ether	295	1·64	102½	..	62	$Cl_{2\frac{1}{2}}H_{\frac{1}{2}}C$	$Cl_2(H_{\frac{1}{2}}Cl_{\frac{1}{2}})C$		
163	Chloral or carbonite of chloroforme (56/29)	200	1·50	74½	..	50	$Cl_{1\frac{1}{2}}H_{\frac{1}{2}}CO_{\frac{1}{2}}$	$Cl(H_{\frac{1}{2}}Cl_{\frac{1}{2}})C_{\frac{1}{2}} + C_{\frac{1}{2}}O_{\frac{1}{2}}$		
164	Bromal or carbonite of bromoforme	260 ?	3·35	..	..	42	$Br_{1\frac{1}{2}}H_{\frac{1}{2}}CO_{\frac{1}{2}}$	$Br(H_{\frac{1}{2}}Br_{\frac{1}{2}})C_{\frac{1}{2}} + C_{\frac{1}{2}}O_{\frac{1}{2}}$		
165	Hydrate of chloral (56/135)	..	..	41¾	..	..	..	$\overline{Cl(H_{\frac{1}{2}}Cl_{\frac{1}{2}})C_{\frac{1}{2}} + C_{\frac{1}{2}}O_{\frac{1}{2}}} + \overline{HO_{\frac{1}{2}}} = 2$ vols.		
166	Monochloride of methylitic ether (71/399)	220	1·31	60	..	46	$ClH_2CO_{\frac{1}{2}}$	$ClH_2C_{\frac{1}{2}} + C_{\frac{1}{2}}O_{\frac{1}{2}}$		
167	Bichloride of methylitic ether	265	1·61	93	..	58	$Cl_2HCO_{\frac{1}{2}}$	$Cl_2HC_{\frac{1}{2}} + C_{\frac{1}{2}}O_{\frac{1}{2}}$		

* [*Sic* in MS.]

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

IV. Organic Compounds (continued).

		Boiling temperature.	Specific gravity.	Gaseous specific gravity. H = 1.	Ditto inferred from specific heat.	Bulk of a molecule.	Chemical analysis.	Chemical arrangement of molecules (hypothesis).	Vapour constants.	
		1.	2.	3.	4.	5.			G.	H.
168	Perchloride of methylitic ether . . .	212°	1·59	64	..	40	$Cl_{1\frac{1}{2}}C_{\frac{1}{2}}O_{\frac{1}{4}}$	$\overline{Cl_2ClC_{\frac{1}{2}}} + \overline{C_{\frac{1}{2}}O_{\frac{1}{2}}} = 2$ vols.		
169	Muriate of benzin (58/319)	0	..	$31\frac{1}{2}$	..	..	$Cl_{\frac{1}{2}}H_{1\frac{1}{2}}C$	$Cl_{\frac{1}{2}}H_{\frac{1}{2}} + \frac{1}{3}(H_3C_3)$		
170	Hydrobromide of benzin (59/364) . .	95	1·52	$53\frac{1}{2}$	..	36	$Br_{\frac{1}{2}}H_{1\frac{1}{2}}C$	$Br_{\frac{1}{2}}H_{\frac{1}{2}} + \frac{1}{3}(H_3C_3)$		
171	Hydroiodate of benzin	135								
172	Oxichlorocarbonic ether (54/228) . .	200	1·13	$54\frac{1}{2}$	..	48	$Cl_{\frac{1}{2}}H_{2\frac{1}{2}}C_{1\frac{1}{2}}O$	$Cl_{\frac{1}{2}}H_{\frac{1}{2}} + H_2C + OC_{\frac{1}{2}}$		
173	Urethane (54/236)	226	1·11	$44\frac{1}{2}$	..	40	$N_{\frac{1}{2}}H_{3\frac{1}{2}}OC_{1\frac{1}{2}}$	$N_{\frac{1}{2}}H_{1\frac{1}{2}} + H_2C + OC_{\frac{1}{2}}$		

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

Appendix I.

Extract from the Proceedings of the Royal Society (vol. 5, p. 604—March 5, 1846).

On the Physics of Media that are composed of free and perfectly elastic Molecules in a state of Motion. By J. J. Waterson (*sic*), *Esq. Communicated by Captain* Beaufort, *R.N., F.R.S.*

This memoir contains the enunciation of a new theory of heat, capable of explaining the phenomena of its radiation and polarization, and the elasticity of various bodies, founded on the hypothesis of a medium consisting of a vast multitude of particles of matter endowed with perfect elasticity, and enclosed in elastic walls, but moving in all directions within that space, with perfect freedom, and in every possible direction. In the course of these motions, the particles must be supposed to encounter one another in every possible manner, during an interval of time so small as to allow of their being considered infinitesimal in respect to any sensible period; still, however, preserving the molecular *vis viva* constant and undiminished.

The author then enters into extensive analytical investigations; first, of the conditions that determine the equilibrium of such a homogeneous medium as is implied by the hypothesis, and of the laws of its elasticity; secondly, of the physical relations of media that differ from each other in the specific weight of their molecules; thirdly, of the phenomena that attend the condensing and dilating of media, and of the mechanical value of their molecular *vis viva;* fourthly, of the resistance of media to a moving surface; fifthly, of the vertical equilibrium of a medium surrounding a planet and constituting its atmosphere; and lastly, of the velocity with which impulses are transmitted through a medium so constituted.

In an Appendix, the author enters into a full explanation of a table of gases and vapours, drawn up with reference to the subjects discussed in his paper.

Downloaded from rsta.royalsocietypublishing.org on August 17, 2013

APPENDIX II.

EXTRACT from the Report of the 21st Meeting of the British Association, Ipswich, 1851. (Transactions of the Sections, p. 6.)

On a General Theory of Gases. By J. J. WATERSTON, *Bombay.*

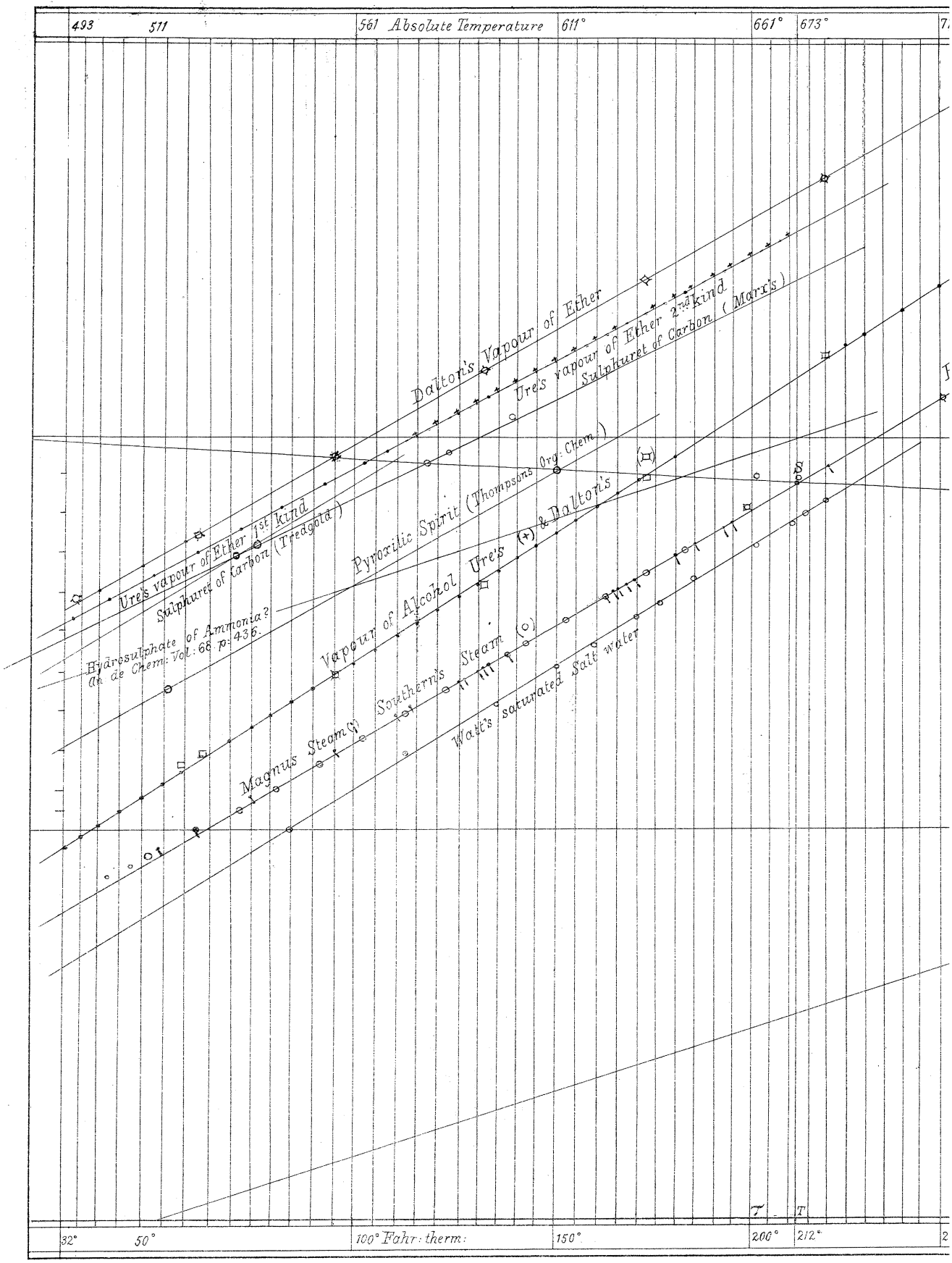
THE author deduces the properties of gases, with respect to heat and elasticity, from a peculiar form of the theory which regards heat as consisting in small but rapid motions of the particles of matter. He conceives that the atoms of a gas, being perfectly elastic, are in continual motion in all directions, being restrained within a limited space by their collisions with each other, and with the particles of surrounding bodies. The *vis viva* of those motions in a given portion of gas constitutes the quantity of heat contained in it.

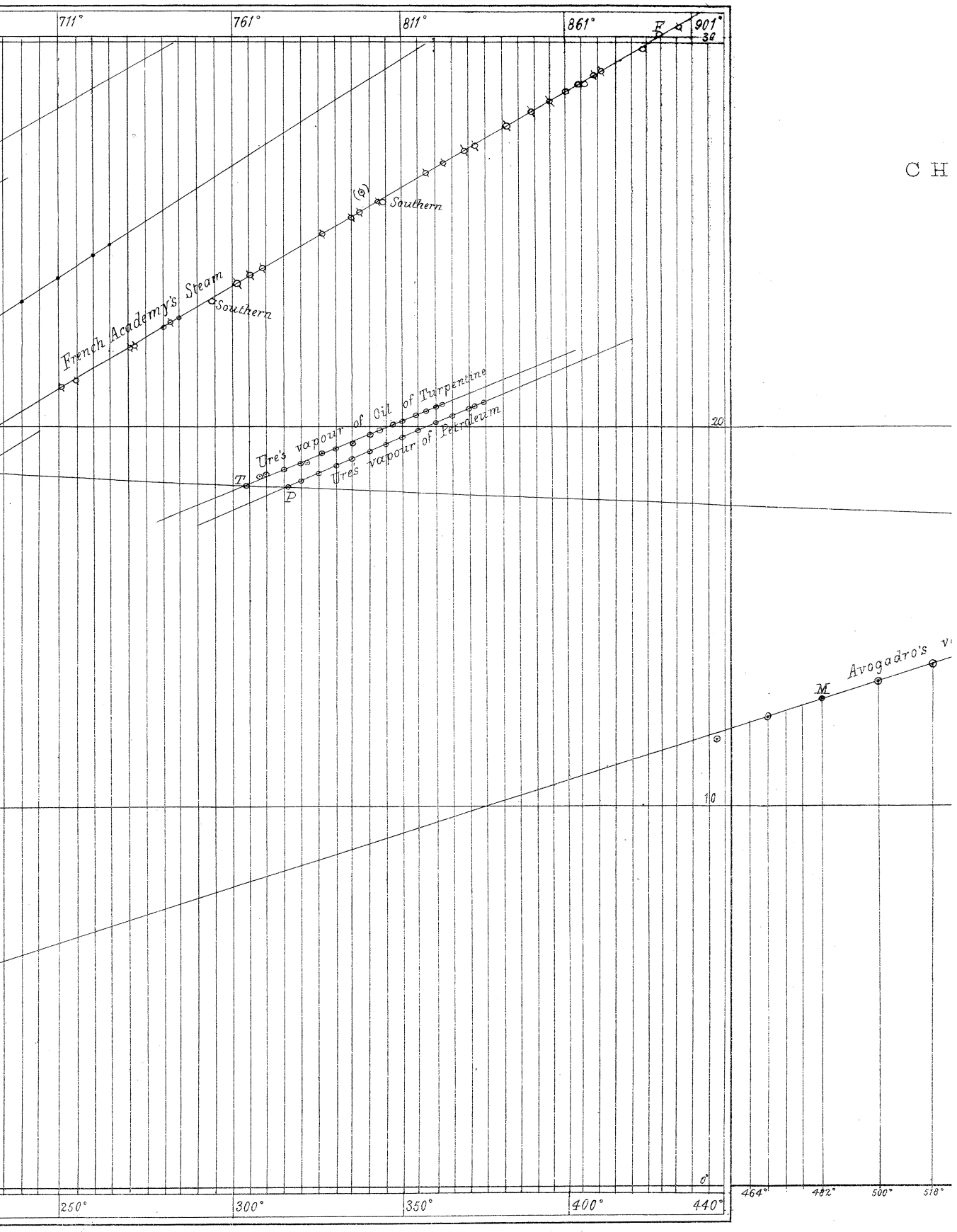
He shows that the result of this state of motion must be to give the gas an elasticity proportional to the mean square of the velocity of the molecular motions, and to the total mass of the atoms contained in unity of bulk; that is to say, to the density of the medium. This elasticity, in a given gas, is the measure of temperature. Equilibrium of pressure and heat between two gases takes place when the number of atoms in unity of volume is equal, and the *vis viva* of each atom equal. Temperature, therefore, in all gases, is proportional to the mass of one atom multiplied by the mean square of the velocity of the molecular motions, being measured from an *absolute zero* 491° below the zero of Fahrenheit's thermometer.

If a gas be compressed, the mechanical power expended in the compression is transferred to the molecules of the gas, increasing their *vis viva;* and conversely, when the gas expands, the mechanical power given out during the expansion is obtained at the expense of the *vis viva* of the atoms. This principle explains the variations of temperature produced by the expansion and condensation of gases—the laws of their specific heat under different circumstances, and of the velocity of sound in them. The fall of temperature found on ascending in the atmosphere, if not disturbed by radiation and other causes, would correspond with the *vis viva* necessary to raise the atoms through the given height.

The author shows that the velocity with which gases diffuse themselves is proportional to that possessed by their atoms according to his hypothesis.

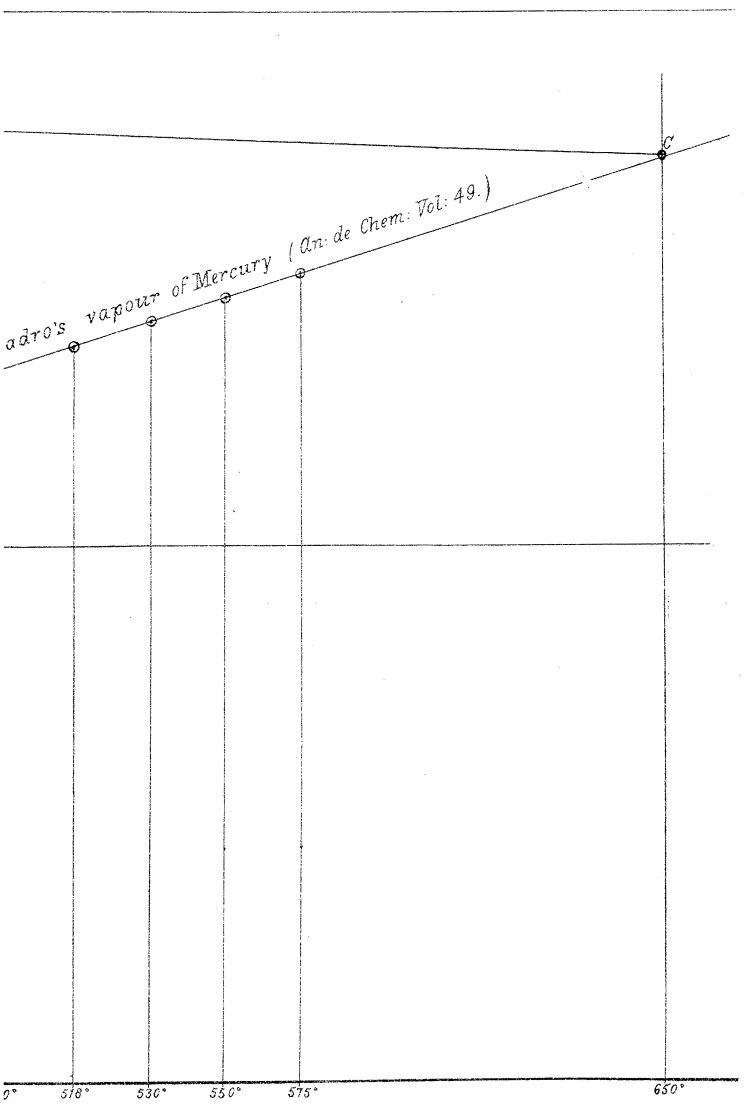
Waterston.


493
511
561 Absolute Temperature
611°
661°
673°
Dalton's Vapour of Ether
Ure's vapour of Ether 2nd kind
Sulphuret of Carbon (Marx's)
Ure's vapour of Ether 1st kind
Sulphuret of Carbon (Tredgold)
Pyroxilic Spirit (Thompsons Org: Chem.)
Hydrosulphate of Ammonia?
Ann de Chem: Vol: 68 p: 436.
Vapour of Alcohol Ure's (+) & Dalton's
Magnus Steam (●) Southern's Steam (○)
Watt's saturated Salt water
T - T
32°
50°
100° Fahr: therm:
150°
200°
212°


711°
761°
811°
861°
901°
30
F
(o) Southern
French Academy's Steam
Southern
Ure's vapour of Oil of Turpentine
Ure's vapour of Petroleum
T
P
20
Avogadro's v
M
10
0°
250°
300°
350°
400°
440°
464°
482°
500°
510°

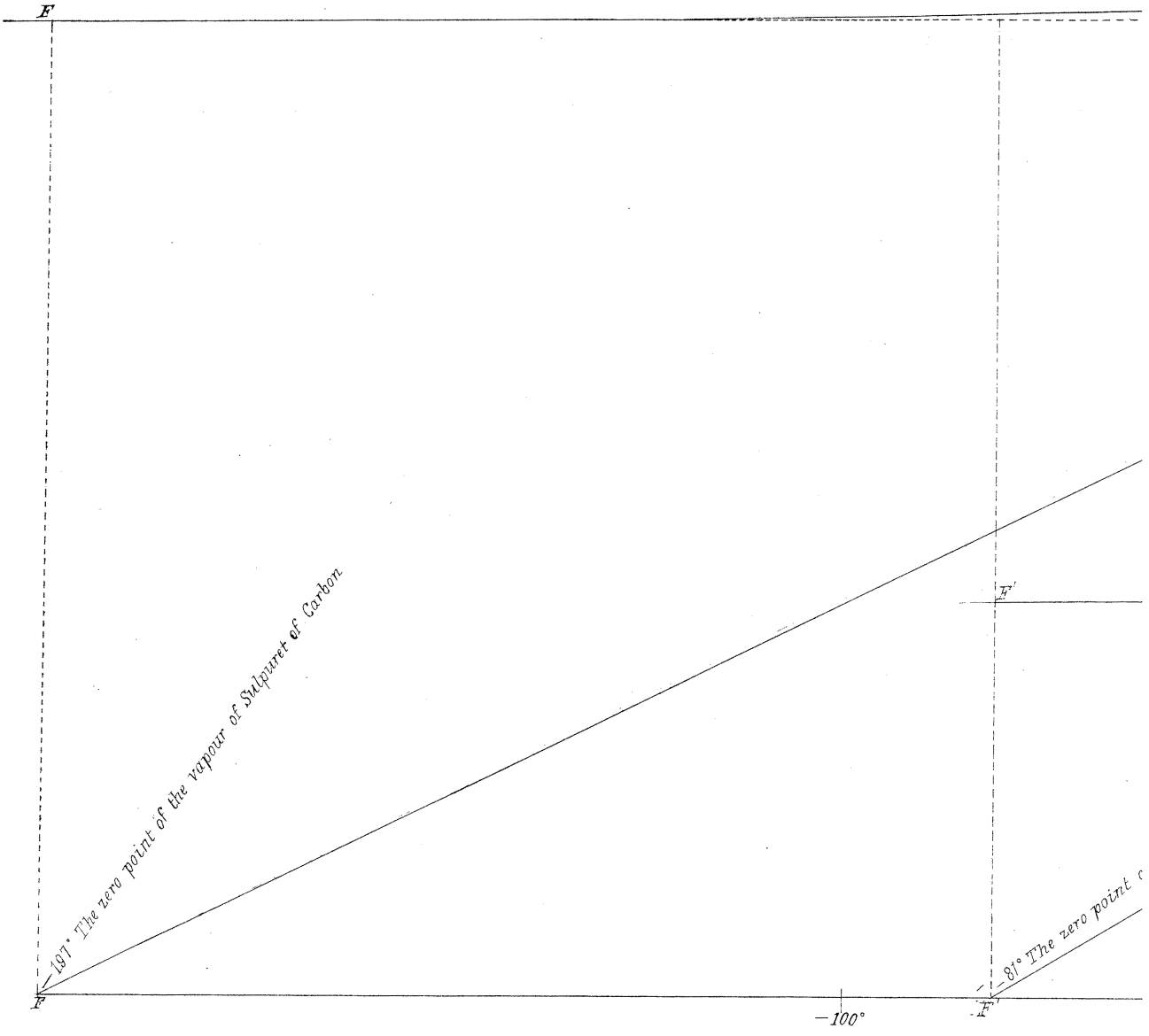
C H

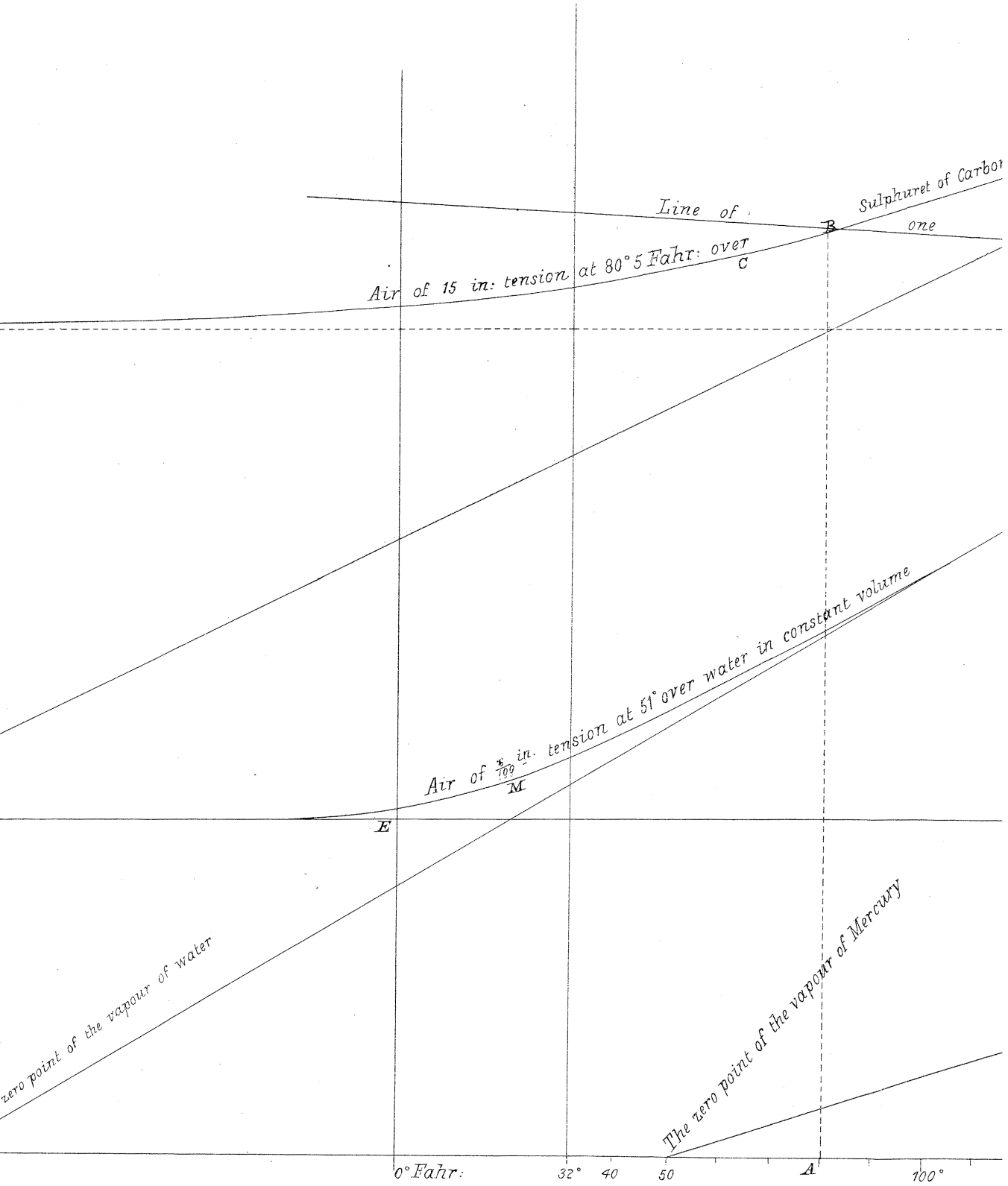
CHART OF VAPOURS
(Oct. 1842.)

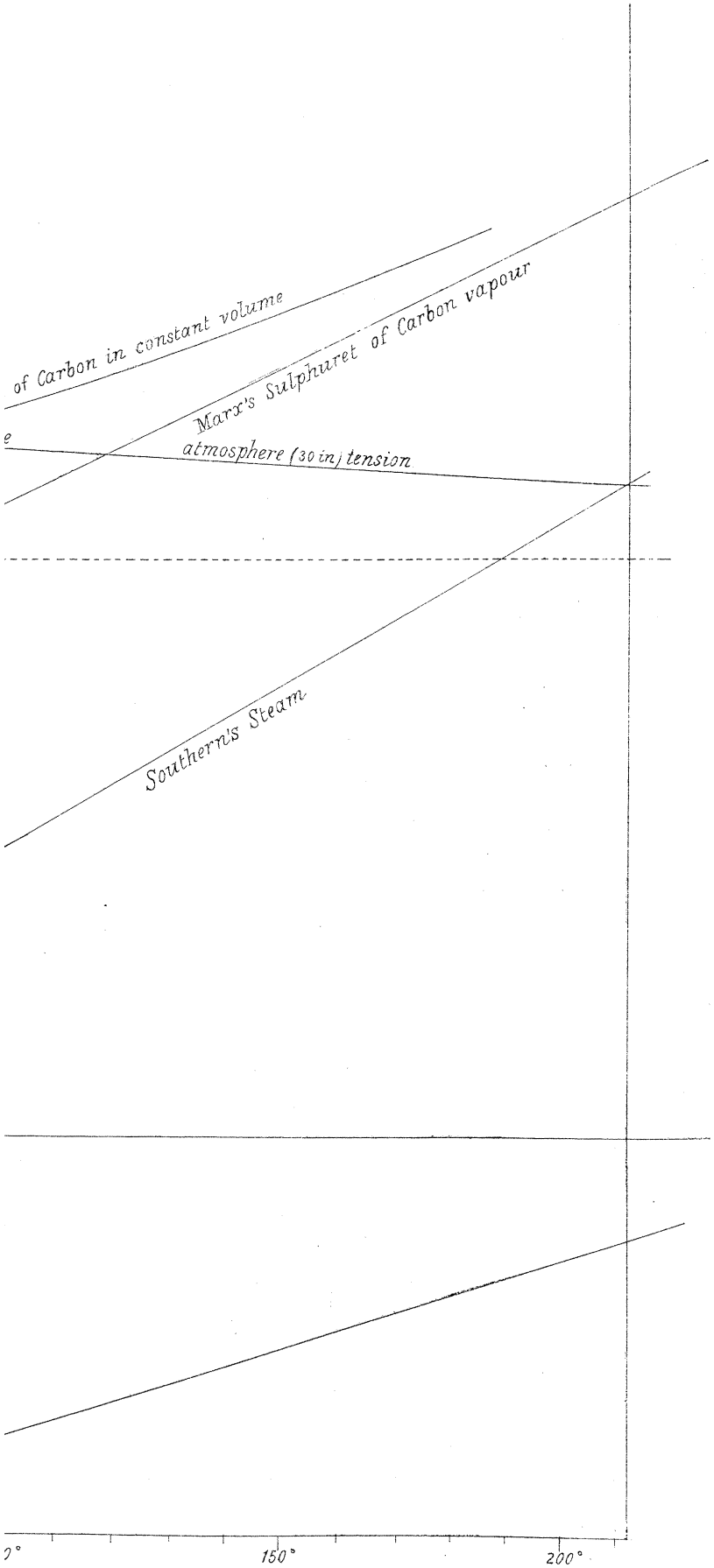


West, Newman lith.

Waterston.


F
F'
F
F'
−197° The zero point of the vapour of Sulpuret of Carbon
−81° The zero point o
−100°


Line of Sulphuret of Carbon
one
B
Air of 15 in: tension at 80° 5 Fahr: over
C
Air of $\frac{5}{109}$ in. tension at 51° over water in constant volume
M
E
zero point of the vapour of water
The zero point of the vapour of Mercury
0° Fahr:
32°
40
50
A
100°



West, Newman lith.

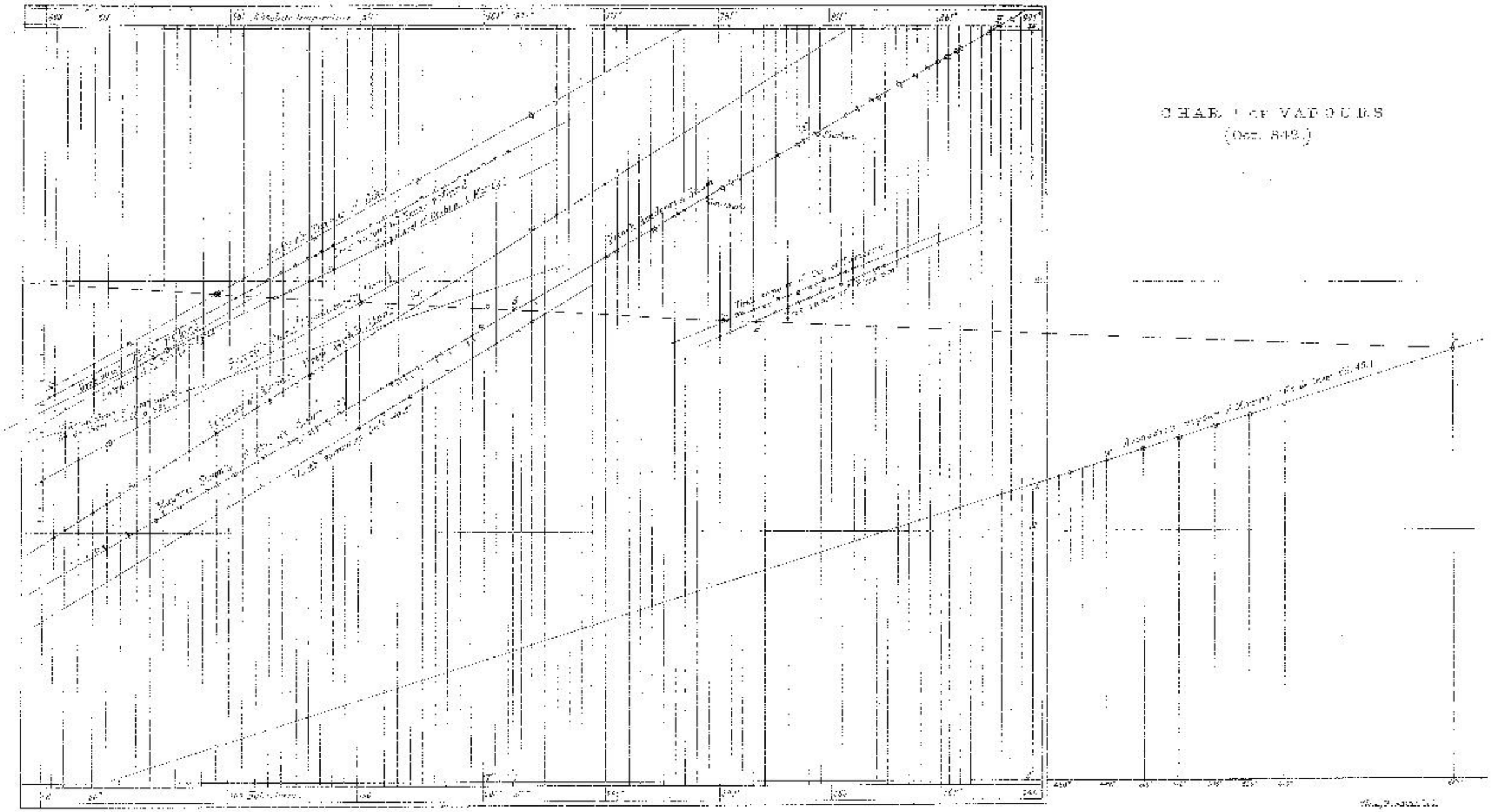
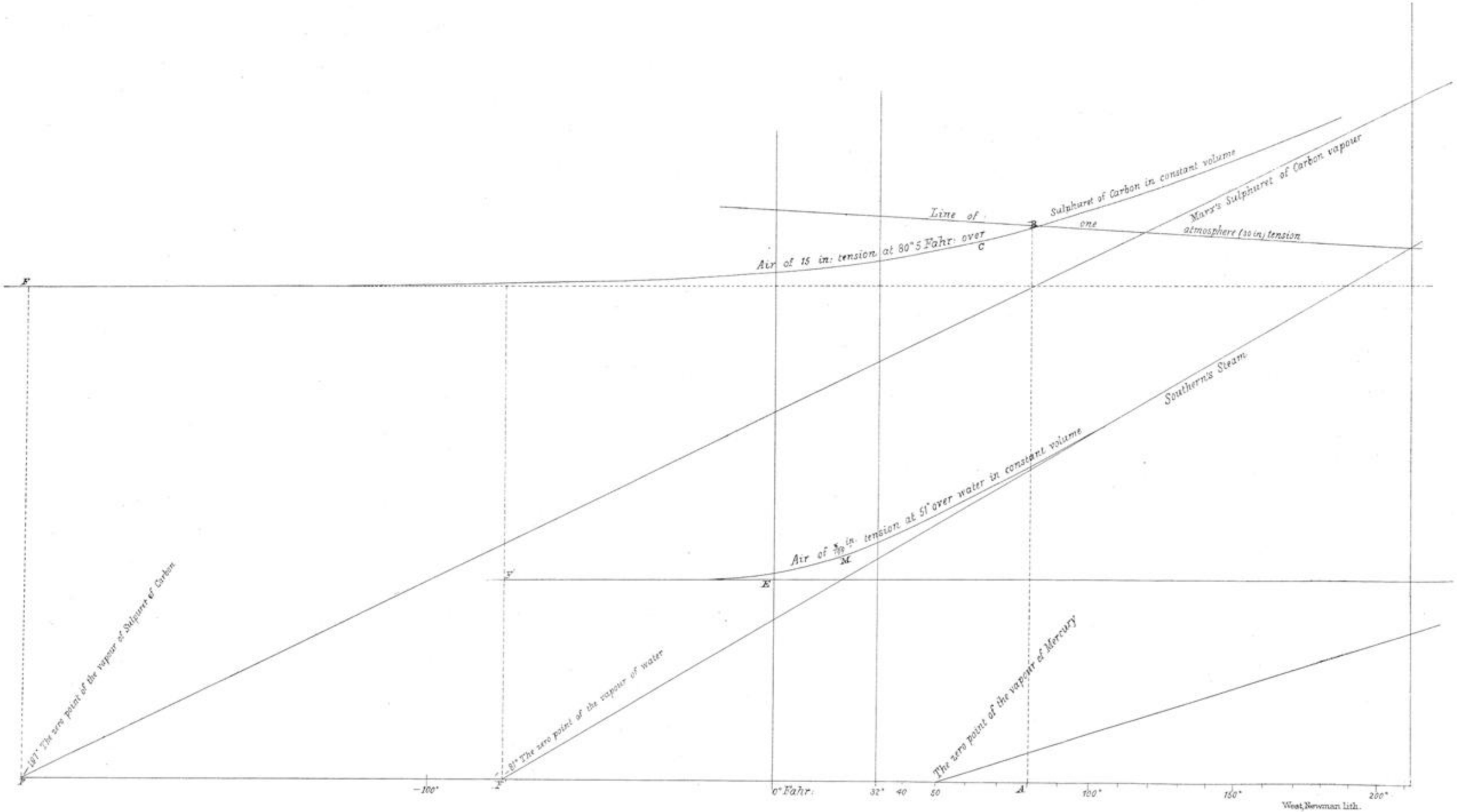


CHART OF VAPOURS
(Oct. 843.)



West, Newman Lith.