ART. X.—*Isothermals, Isopiestics and Isometrics relative to Viscosity;*[*] by C. BARUS.

1. *Historical.*—In the following paragraphs, I endeavor to give a preliminary account of what may be called the isothermals, the isopiestics, and the isometrics with respect to viscosity. Notwithstanding the great geological importance[†] of these relations, nobody has as yet attempted to represent them systematically.

2. *The Material chosen.*—In order to obtain pronounced results for the effect of pressure on viscosity, substances must be selected on which temperature has a similarly obvious effect. For, in addition to the direct access to the molecule which is beyond the reach of pressure, temperature has the same marked influence on the expansion mechanism per unit of volume increment as the other agency. Hence liquids like marine glue, pitch, etc., which change continuously from solid to liquid, and in which this change takes place at an enormously rapid rate and is complete within relatively few degrees, are especially available for the present investigation.

The following data refer to *marine glue.* Viscosity is considered as a physical quality, and apart from such chemical considerations as are introduced in passing from one body to another. I must state, however, that the marine glue can be made to change its viscosity permanently, by cautiously heating it for different lengths of time. Thus I obtained charges

---

[*] Enlarged from a note in the Proc. American Acad., January, 1892.
[†] As has been indicated by Mr. Clarence King, in this Journal for January.

in which, at the same temperature and pressure, the larger viscosities were three or even five times as high as the smaller viscosities, and my work is therefore to this extent independent of the material operated on. Finally marine glue has the advantage of being both adhesive and tenacious, and errors due to slipping (§ 5) are thus reduced as much as possible.

3. *Definitions.*—In my paper* on the absolute viscosity of the three states of aggregation, I defined a fluid (liquid or gas) as a body which, under constant conditions of pressure, temperature, and stress, shows constant viscosity as to time. In a solid *cæteris paribus*, viscosity markedly increases with the time during which stress is brought to bear. The molecular instabilities of a liquid, therefore, are supplied at the same rate in which they are used in promoting viscous motion. In a solid they are used more rapidly than the small rate of continuous supply.

The point of essential concern in these definitions is the constancy of stress, and its value below a certain critical datum. For instance, if in a solid stress be *increased* at the (small) rate necessary to insure a constant supply of instabilities, then solid viscosity will also be constant, and I am by no means sure that in such a case† yield points would eventually present themselves as breaks in the continuity of the solid flow.

On the other hand stress may be conceived to increase so fast, that even a liquid fails to present sufficient instabilities for truly viscous motion. The elasticity and brittleness of many viscous liquids, especially at low temperatures, is a case in point.

4. *Hardness.*—Throughout my work on viscosity,‡ I have adverted to the association of viscosity with zero forces acting for infinite times, and of hardness with infinite forces (relatively) acting for zero times, and have adduced many new examples showing the distinctiveness of these two properties. The subject of hardness has, however, recently taken more definite shape in the researches of Auerbach,§ based on a principle due to Hertz.‖ According to these observers, hardness is an expression for the elastic limits of a body in case of contact between its plane surface and the curved surface of some other (harder) body. Hardness so defined admits of absolute measurement in terms of dynes per square centimeter.

5. *Method of Work.*—In all experiments like the present, one cannot be too careful to preconsider the conditions under

* Phil. Mag., V, vol. xxix, p. 337, 1890. Cf. p. 354.
† Cf. this Journal, III, vol xxxiv, p. 19, 1887.
‡ Phil. Mag., V, vol. xxvi, p. 210, 1888. Cf. Bull. U. S. Geolog. Survey, No. 73, pp. 42–44, 97, 98. 1891. See § 6 below.
§ Auerbach, Wied. Ann., vol. xliii, p. 61, 1891.
‖ Hertz, Crelle's Journal, vol. xcvi, p. 156, 1882.

which the results are obtained; for one is only too apt to attribute an absence of flow to the effect of pressure on viscosity, when the real cause is to be found in the geometry of the apparatus employed. I have therefore availed myself of transpiration methods, since the theory of the experiments is in this case very fully given.

The marine glue, § 2, was forced out of a sufficiently large reservoir, through tubes of steel about 10^{cm} long, and 0·5 to 1^{cm} in diameter, cf. figure 1. Pressures as high as 2,000 atm. were applied at the reservoir, by aid of my screw compressor.* Temperatures between 10° and 30° were kept constant by a suitable water bath. Throughout the work the flow was so excessively slow (amounting to an advance of only a few millimeters per hour), that Poiseuille's law was at once applicable. The only considerable source of error in the work is the occurrence of more or less incidental slipping. However, inasmuch as the outflow of marine glue is capped by a rounded surface, it follows that the flow is most marked at the axis of the tube compatibly with the theory of the experiment. Methods of charging, manipulation, etc., must here be omitted.

Figure 1.—Sectional elevation of the high pressure transpiration apparatus. Scale ½, *E*, steel reservoir; *D*, steel transpiration tube; *C*, charge; *B*, movable solid disc; *A*, compressed oil forced in through the tube *F*.

6. *Volume Viscosity.*—At the end of stated intervals of time (usually hours), the small cylinders of marine glue which had exuded were cut off in the plane of the top of the tube with a sharp knife, and weighed. Now it was curious to note that these cylinders, left to themselves for about a day, showed a gradual and marked deformation, such that the originally plane bottom or surface of section eventually expanded into a symmetrical projecting conoid, with an acute apex angle of less than 45°. I take this to be an example of volume viscosity, inasmuch as an expansion gradually increasing at a retarded
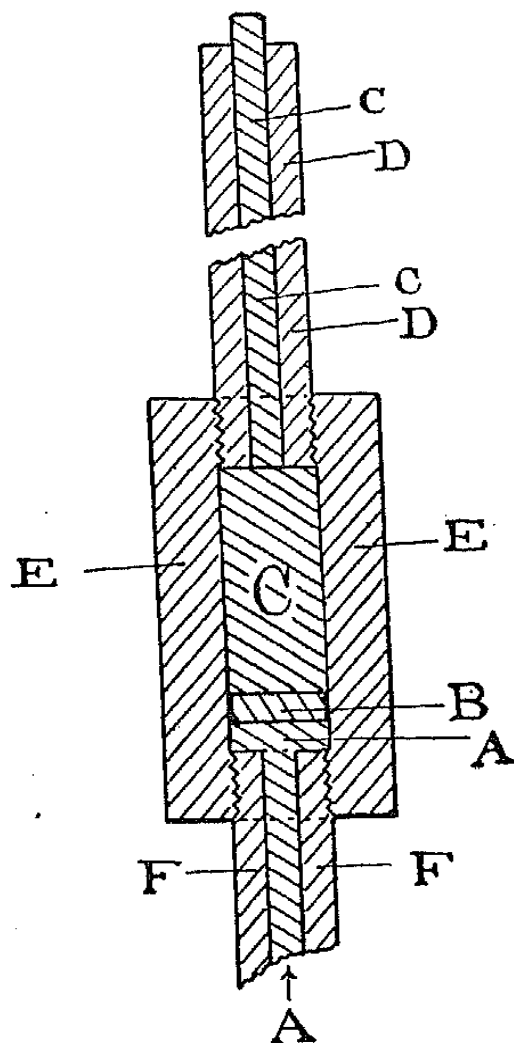
* Phil. Mag., V, xxx, p. 338, 1890.

rate in the lapse of time, is the chief feature. The case, however, is much more complex, for the restitution of volume is greatest in the axis of cylinder where the flow is a maximum, and it is accompanied by a series of distortions of the kind given in figure 2. Here G shows the shape of the cylinder or button immediately after cutting it off of the column H, surrounded by the steel transpiration tube. After 24 hours, when both were left free from pressure, G passed into the form I, and H into K. The emergence of the cone begins visibly, soon after cutting. After long waiting, a cavity sometimes dimples the top of the button as shown at L. I have also obtained cup-shaped deformations, like M. The height of the projecting cone bears no obvious relation to the length of the cylinder. Thus

Figure 2.—Sectional diagrams, showing the elastico-viscous deformations of exuded cylinders of the charge C, Fig. 1, external pressure being zero.

on flat buttons $\cdot 6^{cm}$ in diameter and less than $\cdot 4^{cm}$ high, the apices of the conoids will often be at a distance of $\cdot 3^{cm}$ and $\cdot 4^{cm}$ from the geometric base.

In general, therefore, the originally plane right sections of the transpiring column tend to become plane after stress ceases; or plane right sections of the axially stressed column, tend to bulge out conoidally, symmetrically around the axis, and in a direction opposite to that of the stress, when stress ceases. Thus the experiment points out in a beautiful way how much residual viscosity resembles a slowly reacting elasticity.[*] Complete restitution of form cannot occur because of the dissipation of energy.

7. *Viscosity and Pressure.*—Inasmuch as marine glue is a nonconductor and highly viscous, much time must be allowed before temperature and pressure can be assumed to have penetrated the mass uniformly. Again whenever the oil of the compressor accidentally reaches the transpiration tube, the slip error is enormously increased and the results are worthless. A single charge will not therefore outlast many experiments. These are the chief reasons why much time has to be spent on the work and why it is difficult to coördinate the results. Another annoyance is the unavoidable lack of homogeneity of the charge, and the possibility of a reservoir correction. It will therefore be expedient to briefly indicate the method by which trustworthy results were eventually reached.

[*] A suggestive example of the gradual passage of true elasticity into true viscosity is given by the phenomena observed on stretching a string of (dry) vulcanized india rubber deposited from solution. If the string be suddenly released. elasticity and viscosity appear as the two extreme phases of contraction, terminating a continuous series of intermediate phases.

Table I gives an example of my earlier results. The transpiration tubes were *smooth* internally as shown in figure 1.

The table is one of double entry, and the data contained show the absolute viscosity (η) of marine glue at the stated temperatures and pressures, in terms of one billion g/cs units. The pressure excess is the difference of pressures at the two ends of the tube.

TABLE I.—Mean Values of $\eta/10^9$ for Marine Glue.

Δp = Pressure Excess	100 atm.	300 atm.	1000 atm.	1500 atm.	2000 atm.
Temperature = 8·5°	----	----	>30 000	12·0	>60 000
" = 18·3°	(2·5)	----	8·30	12·0	15·2
" = 22·5°	----	----	1·12	----	2·2
" = 30·5°	·065	·073	----	----	----

Rates at	18·3°	22·5°
$10^{-9} \times \Delta\eta/\Delta p$ =	·0137	·00220
$b = \Delta\eta/\eta_0 \times \tfrac{1}{2}\Delta p$ =	·0091	·020

In constructing the rate of change of viscosity with pressure, I assumed that the whole thread *transpired at the mean of the pressures at the two ends of the steel tube;* or since the pressure at the open end is zero, at half the pressure excess. Furthermore, that

$$\eta_p = \eta_0(1 + bp) = \eta_0(1 + \tfrac{1}{2}b\Delta p)$$

If therefore $\Delta\eta$ be the increment of viscosity corresponding to the pressure $\tfrac{1}{2}\Delta p$, the final data of Table I (rates) are at once intelligible.

What is chiefly striking in this table is the preponderating influence of temperature. Thus the material, which between 20° and 30° C. transpires readily enough, is at 8° so nearly solid, that a burden of 2000 atmospheres, brought to bear at one end of a transpiration tube 10^{cm} long and as wide as 1^{cm}, is unable to produce perceptible flow even after 5 hours. It also appears that *in proportion as the viscosity of a body increases with fall of temperature, its isothermal rate of increase with pressure also increases.*

Some time after, I repeated this work with great care and obtained—

Temperature =	1·8°	·20°	·22°	·24°
$\eta_0 10^9$ =	2·7 } 5·2 }	4·3	·94 } 1·16 }	·28
$b \times 10^8$ =	8·0 } 3·0 }	1·3	3·9 } 1·8 }	4·8

It would be premature to speculate on the nature of the relation of viscosity to pressure and to temperature, on the basis of these results. As to the pressure coefficient b, one

can only infer that its value is of the order of ·005, and that it bears no obvious relation to the initial viscosity, or to temperature.

In endeavoring to improve upon this work I cut a screw thread in the *inside* of the transpiration tube and thus largely obviated slipping, by compelling the charge to flow on itself. I also made all observations in triplets, including each measurement at a high pressure or temperature between two fiducial measurements at a given lower pressure or temperature. Only such observations were taken for which the fiducial data were identical. Finally by treating the charges individually, I found that although the viscosities at the same temperature were very different, the pressure coefficients followed each other in the order of the initial viscosities.

Experiments made in this way showed—

Temperature =	16·5°	13·9°	11·9°	18·0°	15°	15°	20°
$\eta_0/10^9$ =	·50	2·15	2·50	·70	3·7	3·7	·40
$b \times 10^3$ =	4·2	4·3	8·9	5·3	4·6	4·8	6·5

These are the best results I have been able to obtain. How nearly linear the variation of viscosity with pressure is, may be seen in the following example of consecutive measurements :

Pressure excess Δp =	340	700	1055	1410	1770	340	*atm.*
Viscosity, $\eta/10^9$ =	·87	1·20	1·60	2·07	2·30	·87	*g/cs*

Even in case of high viscosity ($> 10^{10}$), a tendency of viscosity to increase at an accelerated rate with pressure is only vaguely apparent, e. g.,

Pressure excess, Δp =	505	1020	505	1540	1022	1540	*atm.*
Viscosity, $\eta/10^9$ =	8·4	12·6	7·9	17·9	12·9	17·1	*g/cs*

Taking the above work as a whole, therefore, I am bound to infer that within the range of observation (2000 atm.), the pressure coefficient is constant : for though varying between ·004 and ·009, it shows no discernable relation to the initial viscosity (η_0 for Δp = 0), or to temperature. In other words, to assume that the rate at which viscosity increases with pressure at any temperature, is proportional to the initial viscosity at that temperature, is the nearest approach to the actual state of the case which my observations enable me to make. Taking the mean of all values in hand I thus obtain—

$$\eta_{\theta,\,p} = \eta_{\theta,\,0}(1 + \cdot0057\,p) \qquad (1)$$

where the subscripts show the temperature (θ) and pressure (p) at which viscosity (η) is taken ; and where p is the mean of the pressures at the two ends of the transpiration tube.

8. *Viscosity and Temperature.*—It is next in place to find a suitable expression for the relation of viscosity to temperature. Contrary to my expectations this was comparatively easy; and the reason seems to be that so long as pressure is constant, the error due to slipping is less liable to change. An example of the results worked out from triads as above, and obtained with screw tubes is given in the following tables. $\Delta p = 505$ *atm.*

Temperature	Observed. $\eta/10^9$	Computed. $\eta/10^9$		Temperature	Observed. $\eta/10^9$	Computed. $\eta/10^9$	
12°	7·70	7·78	$A=11\cdot895$	15°	8·15	8·13	$A=12\cdot385$
14°	3·75	3·61	$B=\ \cdot167$	17°	3·82	3·80	$B=\ \cdot165$
16°	1·61	1·67	$\eta_0=7\cdot8 \times 10^{11}$	19°	1·72	1·78	$\eta_0=2\cdot4 \times 10^{12}$
				21°	·81	·83	
				23°	·42	·39	

It is seen at once that within the range of observation (12°–16° C., 15° to 23° C.) temperatures increase in arithmetical progression while viscosities decrease in geometrical progression. Hence (2) $\log \eta_{p,\,\theta} = \log \eta_{p,\,0} - B\theta$, and the factor B has the large value, ·165. Of the two sets of data given, the initial viscosity, $\eta_{p,0}$ is fully three times larger in one case than in the other. Nevertheless the quantity B is practically the same in both. For this reason I shirked the great labor attending experiments at higher pressures and concluded conformably with the suggestions of the preceding paragraph, that as a first approximation the rate at which viscosity increases with temperature at the temperature $\theta°$, is proportional to the viscosity at $\theta°$, and is independent of pressure.

9. *Summary and chart.*—With the principle thus laid down I am able to give a graphic exhibit of the isothermals and the isopiestics. This is done in the chart, figure 3, where the ordinates are absolute viscosities, and the abscissas, pressures and temperatures respectively. The isopiestic for $p = 250$ atm. is directly observed between 15° and 23°. The other curves are computed from this by aid of the coefficients deduced in §§ 7, 8. The range as a whole may be taken as that of the present experiments. The (computed) initial viscosity $\eta_{0,\,0}$ (for $p = 0$ and $\theta = 0$) is very nearly 10^{12}. As usual $p = \Delta p/2$.

10. *Isometrics.*—From these data the isometrics may be constructed graphically and in this way the curves marked η were obtained. I am now able to answer some important questions as to how temperature and pressure must vary, in order that viscosity may remain constant. Equations (1) and (2) lead easily to

$$(dp/d\theta) = (ln\ 10)\ B(1 + bp)/b \qquad (3)$$

Hence the isometrics are all identical as to contour and ob-

tained by dropping the initial curve over stated amounts. For any viscosity and at any temperature within the range of observation, therefore, the increment of pressure which will just annul the decrement of viscosity due to a rise of temperature of one degree Centigrade is, for instance,
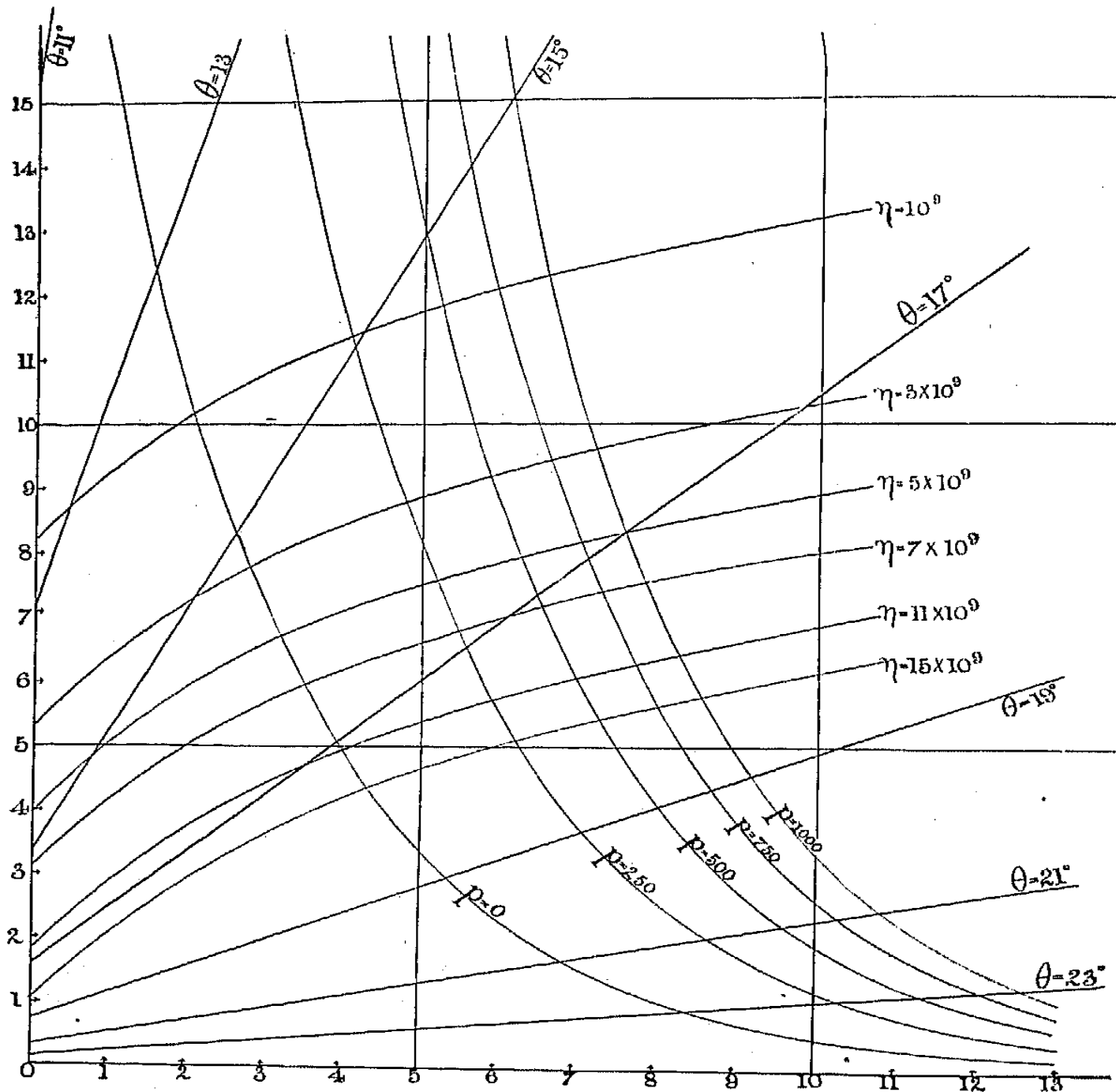

Fig. 3.

Fig. 3.—Chart showing the isothermals (θ), the isopiestics (p), and the isometrics (η), relative to the viscosity of marine glue.

Abscissas: Pressure in *hundreds* of atmospheres, or in *two hundreds* of atmospheres of pressure excess.

Temperatures in degrees Centigrade beginning with 10° C.

Ordinates: Viscosities in *billions* of absolute (g/cs) units.

Temperatures in degrees Centigrade beginning with 10° C.

Pressure   =   0 atm.   500 atm.   1000 atm.
Increment of pressure = 67 atm.   256 atm.   380 atm.

and so on. Thus the relative inefficiency of pressure as compared with temperature is apparent, though to make the comparison just, both agencies should be taken per unit of volume increment. Cf. § 11.

11. *Digression, Logarithmic isothermals.*—Believing that the error due to slipping increases with pressure, i. e. in proportion as the charge becomes more solid, and noting the tendency (§ 7) of isothermals for high viscosity to slope upward, I thought it worth while to compute the isothermals on the supposition that $\log \eta = a' + b'p$, as an extreme case. Necessarily, marked violence is thus done to the observations, and b' obtained from high pressures must be smaller than b' from low pressures. Preferring the latter, I found, for instance

$\eta_0/10^0$	=	·69	5·9	4·7	2·9	·64
$b' \times 10^5$	=	81	73	93	73	74

As before a dependence of b' on η_0 does not appear and $b' =$ ·00078 may be taken as the mean value.

The interest which attaches to this case is its bearing on the isometrics, which now appear as straight lines. For if

$$C = \eta_{\theta p}/\eta_{00}, \quad \log C + B\theta = b'p, \quad \text{and} \quad (dp/d\theta) = B/b' = 210$$

In other words 210 atm. would annul the decrement of viscosity produced by a rise of temperature of 1° C., at all temperatures and pressures.

Seeing that in an elegant research of Ramsay and Young,[*] and in high pressure work[†] of my own, the volume isometrics of liquids appear as straight lines, the present considerations may possibly claim more than passing comment.

The immediate object of the present paragraph, however, is to give warrant to the statement, that in high pressure phenomena *at least* 200 atm. must be allowed per degree Centigrade, in order that there may be no change of viscosity.

12. *Maxwell's theory.*—If for the sake of definiteness, viscosity (η) be defined as proportional to the ratio $(N-n)/n$, of the number of stable configurations $(N-n)$, to the number of unstable configurations (n), in a given volume, then the above expressions may easily be translated into the language of Maxwell's theory of viscosity.[‡] I shall therefore withhold further remarks here. The conditions are simplified since for

---

[*] Ramsay and Young: Phil. Mag., xxiii, p. 435, 1887 ; xxiv, p. 196, 1887.
[†] Barus: Phil. Mag., xxx, p. 338, 1890.
[‡] This was done in my note in this Journal for September, p. 255.—In the series, atom, molecule, viscous configuration, the last can not be as sharply defined as the other two, and only the former as yet admits of generic classification (periodic law). Cf Am. Chem. Journ., xiv, pp. 197–201.

a substance like marine glue, n is probably small as compared with N.

13. *Measurement of excessively high pressure.*—Let there be given a tube of length l and radius ρ. Let $\eta = \eta_0(1 + bp)$ be the viscosity of the viscous liquid forced through it by the pressure excess $\Delta p = 2p$ (so that there is no pressure at one end of the tube), and at the constant temperature θ. The length (λ) of a cylinder of fluid issuing per unit of time (t) will then be $\rho^2 \Delta p / 8 l \eta_0 (1 + b \Delta p / 2)$. Hence if negative pressures be excluded, the function λ/t is of a kind which continually increases with Δp, a state of the case which would not be true if the expression of § 11 were applicable.

In view of the observed property of λ/t, it is worth inquiring in how far the transpiration method is available for high pressure measurement, when most other means fail.

Take for example a tube $\frac{1}{16}$ inch in diameter and 1 inch long. Then the mass m of the above marine glue which at say 18° would exude per hour is

$m \times 10^6 =$	5970	7550	7810	7900	7950 *grams.*
Δp $=$	1000	5000	10000	15000	20000 *atm.*

where $\eta = 10^9(1 + \cdot 00285 \Delta p)$.

Thus it appears that whereas a hole $\frac{1}{16}$ inch in diameter may be efficiently sealed by marine glue at 18° C., pressure measurement by aid of the exuding mass is impossible above 10,000 atm., whereas even between 5000 atm. and 10,000 atm. the method is insensitive. To use a method like the present for very high pressure measurement, a substance of smaller pressure coefficient must therefore be sought, if such a one with other necessary qualities, exists. It is with the object of searching for such a body, as well as of finding the maximum of hydrostatic pressure attainable in the laboratory that I had a tinned screw and socket constructed,* and hope to be able to report the results of my work at an early opportunity. To my knowledge the only other gauge available under the circumstances is the one I based on the resistance of mercury. It is sufficient, however, for making the comparisons in question.

Phys. Lab. U. S. Geolog. Survey, Washington, D. C.

---

* Proceed. American Acad., xxv. pp. 94, 108, 1890.