

**FLUIDITY AS A FUNCTION OF VOLUME, TEMPERATURE AND  
PRESSURE. THE EQUATION OF STATE, AND THE  
TWO KINDS OF VISCOUS RESISTANCE SO-  
CALLED "SLIPPING" OF GASES.**

[PRELIMINARY.]

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**Fluidity and Volume.**

Attention<sup>2</sup> has been repeatedly called to the intimate relationship which exists between the fluidity of a liquid and its volume. Batschinski<sup>3</sup> has recently given this relationship quantitative expression. According to him

$$\eta = c/v - w$$

where  $\eta$  is the viscosity of the liquid,  $v$  the specific volume, and  $c$  and  $w$  are characteristic constants for the given liquid. In terms of the fluidity  $\varphi = 1/\eta$ , we have

$$v = w + c\varphi \tag{1}$$

or, the volume is a linear function of the fluidity,  $w$  being the *limiting volume* toward which the volume approaches as the fluidity approaches zero. If, following Batschinski, we call  $v - w$  the *free volume*, the law may be stated in the very simple form, *the fluidity of a liquid is directly proportional to its free volume*. Batschinski has found remarkable agreement between the observed and calculated viscosities for a large number of liquids, it apparently making no difference whether the change of volume is produced by altering the temperature or the pressure. For a range of temperature extending from 0° to the boiling point, or even beyond the ordinary boiling point, the differences seldom exceed 1%, except with associated substances such as the alcohols, which are exceptional, here as elsewhere.

The above law is really an extension of the law already given,<sup>4</sup> expressing the relation between the fluidity of a suspension and its volume concentration. The volume concentration of the medium,  $c_2$ , in which the fluidity of the suspension becomes zero, corresponds to the volume where the fluidity becomes zero in pure liquids. If  $m_2$  represents any volume concentration of the medium, then  $m_2 - c_2$  corresponds to the free volume,

<sup>1</sup> For earlier papers of the author on this general subject (cf. *Phys. Rev.*, **35**, 407 (1912)); [2] **1**, 96 (1913); *Z. physik. Chem.*, **83**, 641 (1913); *Trans. Chem. Soc.*, **103**, 959 (1913); *J. Phys. Chem.*, **18**, 157 (1914); *J. Ind. Eng. Chem.*, **6**, 233 (1914).

<sup>2</sup> *Am. Chem. J.*, **35**, 215 (1906); **43**, 290 (1910); **45**, 268 et seq. (1911); *Z. physik. Chem.*, **83**, 655 (1913).

<sup>3</sup> *Ann. de la Soc. d'encouragement de sciences experimentales et des leurs applications du nom de Christophe Ledensoff, Suppl.*, **3** (1913); *Z. physik. Chem.*, **84**, 643 (1913).

<sup>4</sup> *Phys. Rev.*, **35**, 421, et seq. (1912).

and the fluidity of the suspension is directly proportional to the free volume. From equation (9)<sup>1</sup> of an earlier paper by the author we get,

$$\varphi = (m_2 - c_2)\varphi_2/c_1 \quad (2)$$

which is evidently a more explicit form of equation (1) above. In suspensions the medium has a finite fluidity, hence the fluidity of the suspension  $\varphi$  cannot exceed the fluidity of the medium  $\varphi_2$ . Pure liquids may be regarded as suspensions in space, of infinite fluidity, so that there is apparently no limit to the fluidity which may be obtained by indefinitely increasing the volume. A further point of interest in this connection, is the fact that the concentration of its zero fluidity in a suspension, is independent of the temperature or of the nature of the medium.

### The Equation of State.

If, in van der Waals' equation,

$$(p + a/v_2)(v - b) = RT,$$

we substitute for the volume its value in terms of  $w + c\varphi$ , we obtain a formula in which the fluidity, temperature and pressure are variables. Since, however, the pressure is constant under the usual conditions of viscosity measurement, this relation becomes

$$T = A\varphi + C + B/\varphi + D - E/(\varphi + D)^2 \quad (3)$$

in which A, B, C, D and E are constants. Over any ordinary range of temperature, this formula may be simplified. In fact, the author has already shown<sup>2</sup> that the formula

$$T = A\varphi + C - B/(\varphi + D) \quad (4)$$

will reproduce the observed fluidities of all the liquids tested with very great accuracy. For all but the most highly associated liquids, or over a very wide range of temperature, the formula may be still further simplified to

$$T = A\varphi + C - B/\varphi \quad (5)$$

and satisfactory results obtained. Thus for seventy substances, the average deviation between the observed and calculated values of the absolute temperature is only 0.09%. For a highly associated substance like water, the average deviation is 0.17%, but with Formula (4) it becomes only 0.01%.

In a similar manner one obtains a formula for the pressure in terms of the fluidity

$$p = \alpha T/(\varphi + \beta) - \gamma/(\varphi + \delta)^2. \quad (6)$$

When the fluidity or the temperature is very great, the second term of the right-hand member becomes negligible and the formula represents an equilateral hyperbola. Large fluidities and high temperatures presum-

<sup>1</sup> *Phys. Rev.*, **35**, 423 (1912).

<sup>2</sup> *Z. physik. Chem.*, **66**, 251 (1909).

ably belong to the gaseous state and, as van der Waals' equation applies best to gases where the volume and temperature are great, we might look for a similar fluidity relation. That any such expectation is doomed to disappointment is proved by Clerk Maxwell's observation that the fluidity of a gas over a short range of pressures and temperatures is independent of the pressure, which has been repeatedly confirmed. Thus Equation (1) applies to liquids but certainly not to rarefied gases. The cause of this interesting peculiarity may well engage our attention next.

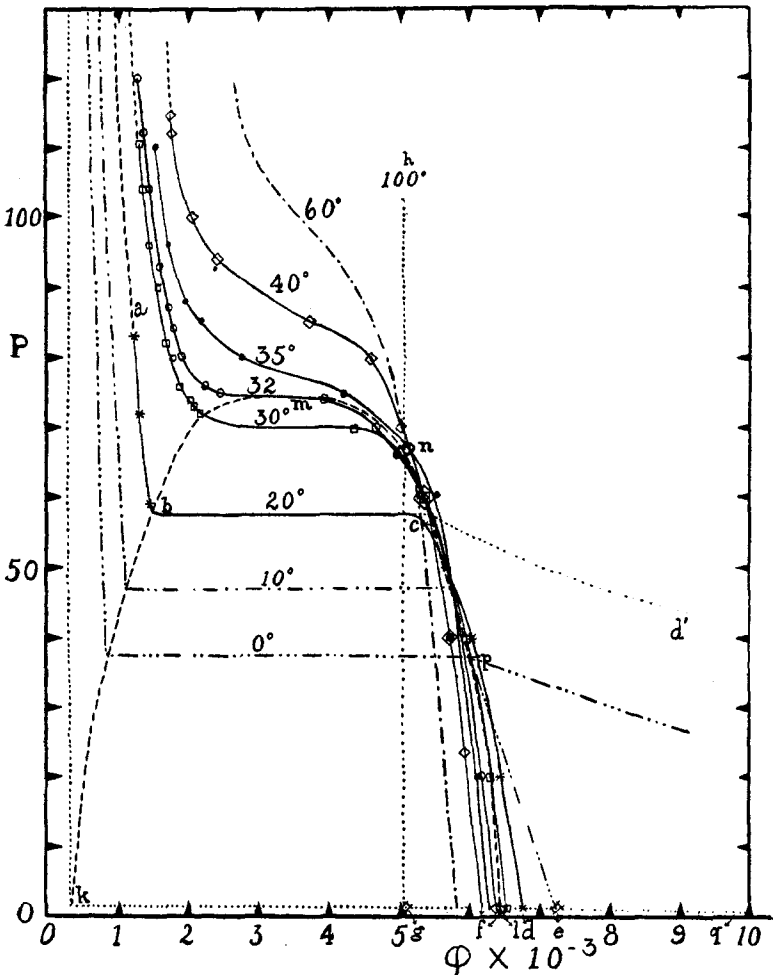


Fig. 1.—Pressure-fluidity curves of carbon dioxide.

In Fig. 1 are drawn the pressure-fluidity curves for carbon dioxide for the temperatures measured by Phillips.<sup>1</sup> The curves are drawn as

<sup>1</sup> *Proc. Roy. Soc. (London)*, 87A, 48 (1912).

continuous lines between the observed points. The broken lines have been added for diagrammatic purposes. The left half of the figure, which corresponds to low fluidity and temperature, presents a striking similarity to the familiar pressure-volume diagram. At the highest pressures, the fluidity is not greatly affected by a change in the pressure, *e. g.*, at  $32^{\circ}$  and a pressure of 120 atmospheres, a lowering of the pressure by four atmospheres causes an increase in the fluidity of less than 4%. At a lower pressure the fluidity is extremely susceptible to changes in pressure, a lowering of the pressure by four atmospheres at 76 atmospheres, causing an increase in the fluidity of a full 100%. Both the gaseous and liquid phases are present in the region inside of the Curve *kbmcl*. The right side of the figure is quite different from the familiar pressure-volume diagram. Instead of the fluidity being highly susceptible to changes in pressure, it is but slightly affected, *e. g.*, at  $32^{\circ}$  and 50 atmospheres pressure, a lowering of the pressure by four atmospheres causes only a 10% increase in the fluidity. Let us now consider carbon dioxide at  $20^{\circ}$  which is well below the critical value. At high pressures the fluidity increases linearly from *a* to *b*; there is then a sudden increase in the fluidity from 1500 to 5300 C. G. S. units, as the substance passes from the liquid to the gaseous condition. We should expect the fluidity to continue to increase as the pressure is further lowered, giving the Curve *cd'*, but the curve actually obtained is *cd*. It is generally true that the fluidity of liquids increases with the temperature, while, on the other hand, the fluidity of gases decreases with the temperature, hence the pressure-fluidity curves for different temperatures must cross each other. It is interesting to note that the figure shows, that not only is this true, but, when the temperatures are sufficiently high, the curves all tend to pass through a particular point *n*; and for lower temperatures, the curves tend to intersect each other on the Curve *ncl*.

The fluidity of carbon dioxide at atmospheric pressure for  $0^{\circ}$ ,  $40^{\circ}$  and  $100^{\circ}$ , as obtained from the Tabellen of Landolt, Börnstein and Meyerhoffer, are plotted at the points *e*, *f*, and *g*, respectively. If *gnh* is taken to represent the hypothetical pressure-fluidity curve of carbon dioxide at  $100^{\circ}$ , it is evident that, for this temperature, Maxwell's law holds perfectly so that the fluidity is independent of the pressure. But is it equally evident that it would hold strictly for no other temperature. At  $0^{\circ}$  the fluidity curve of gaseous carbon dioxide is approximately *pe*, while for the temperature of the ordinary boiling point of carbon dioxide the pressure-fluidity curve would apparently be *lq*, and the law breaks down entirely. What would happen if the temperature were raised far above  $100^{\circ}$  would be very interesting to learn, but the data are not available at present.

#### The Nature of the Two Causes of Viscous Resistance.

That the pressure-fluidity curves do not follow an equation of the van der Waals type as the fluidity increases, may be due to the appearance

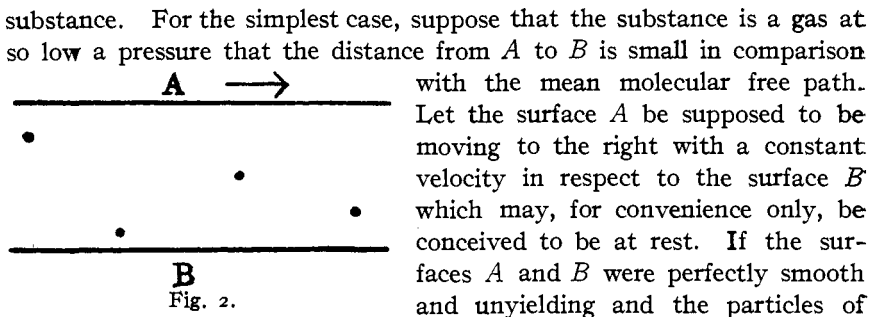
of a new cause of resistance. We must therefore now inquire more particularly into the nature of viscous resistance. It has long been realized that a cause of viscous resistance in gases arises from the diffusion of the particles of layers with high translational velocity into layers whose translational velocity is lower, and *vice versa*. According to this explanation the loss of translational velocity must increase with the temperature, which accords with the fact that the fluidity of a gas decreases as the temperature is raised.

But in liquids the fluidity *increases* as the temperature is raised and it appears that there is a second cause of viscous resistance which has been repeatedly attributed to the attraction between the molecules. Batschinski<sup>1</sup> gives this conception expression in the following terms: "In gases, the properties which depend upon the reciprocal attraction of the molecules manifest themselves only slightly, whereas with liquids, on the contrary, these properties are of prime importance. If we may think of two parallel layers of the liquid as of two rows of men, the men moving in the place of molecules, we must require these men to take hold of their nearest neighbors and to hold them for a time."

This explanation seems to the present author to be inadequate for the following reasons: As a particle *A* comes within the range of attraction of a particle *B* in an adjacent layer supposed to be moving more slowly, the particle *A* will be accelerated and only after passing *B* will the retardation take place. I see no reason why these two actions should not exactly neutralize each other, in which case none of the translational energy will be changed into heat. But, perhaps it would be urged that the retarding influence is more like chemical combination, since the particles lay hold on each other and, in the words of Batschinski, "während einiger Zeit festhalten." If the particles of the liquid grasp and hold each other, a kind of association must result which should be detected by some physical method, and non-associated substances ought not to show any viscosity at all. As a matter of fact, not only do all liquids have viscosity, but mercury, which is usually regarded as non-associated, has a lower fluidity than many highly associated substances such as water and alcohol. This objection may be avoided by assuming that this grasping and holding of the particles is proportional to the rate of shear of the liquid, so that it is zero when the liquid is at rest; but, since the molecules are always in rapid vibrational motion, it is difficult to see how the small translational motion would affect the attraction in a way to produce the result which we observe.

In order to get a clearer idea of the nature of the two causes of viscous resistance to flow, let *A* and *B* in Fig. 2 represent two parallel planes at a constant distance apart, the space between being filled with the viscous

<sup>1</sup> *Loc. cit.*



substance. For the simplest case, suppose that the substance is a gas at so low a pressure that the distance from *A* to *B* is small in comparison with the mean molecular free path. Let the surface *A* be supposed to be moving to the right with a constant velocity in respect to the surface *B* which may, for convenience only, be conceived to be at rest. If the surfaces *A* and *B* were perfectly smooth and unyielding and the particles of fluid perfectly elastic spheres, we would not have a model of viscous flow; for as the particles collided with these surfaces, the angle of rebound would in each case be equal to the angle of impingement and since there is conservation of momentum, no translational motion could be transmitted to or from the walls, *i. e.*, the "slipping" would apparently in this case be perfect. In order to obtain a model of viscous flow, we are therefore obliged to make some assumption, and the simplest and most probable one is that the surfaces *A* and *B* are not perfectly smooth. In view of the known discontinuity of matter, the least degree of roughness that we could well assume, is that the surface is made up of equal spheres, all of whose centers lie in the same plane and as closely packed together as possible. That there is a greater degree of roughness in all ordinary surfaces is probable, but it suffices for our present purposes to show that this simple assumption in regard to the nature of the surfaces gives a workable model of viscous flow. In a model of viscous flow it is necessary for the molecules striking the surface *A* to be given a component of velocity in the direction of the viscous flow. We shall refer to this as *translational* velocity in contradistinction from the disordered *vibrational* velocity of the molecules. The resultant translational velocity of the molecules is evidently proportional to the rate of efflux, while the *resultant* vibrational velocity is zero. It is further necessary that as the molecules strike the surface *B*, the translational velocity received at *A* should be transformed into vibrational velocity or heat, so that any resultant translational velocity would disappear in a short time were it not continually supplied at the surface *A*.

That the model described above meets these requirements depends upon the truth of the following theorem: *When a series of elastic particles strike a rough surface, the resultant component of velocity along the surface will be diminished.* That this is true must now be made evident. Let *M*, *N*, and *P*, in Fig. 3 represent the section through the centers of three of the greatly magnified spheres supposed to make up the surfaces in Fig. 2. Suppose that a small particle were to strike such a surface at any acute angle  $\theta$ . It is evident that if such a particle is to strike the

sphere  $N$  in the plane of the paper, its possible paths all lie between  $A$  and  $G$ . By drawing the directions of the particle before and after collision, assuming that the angle of rebound at any point of the surface is equal to the angle of impingement, we find that for possible paths between  $B$  and  $D$  the average resultant velocity of rebound is exactly opposite in direction, although diminished in amount. For paths between  $A$  and  $B$  a particle would collide with  $M$  on rebounding from  $N$  but the component

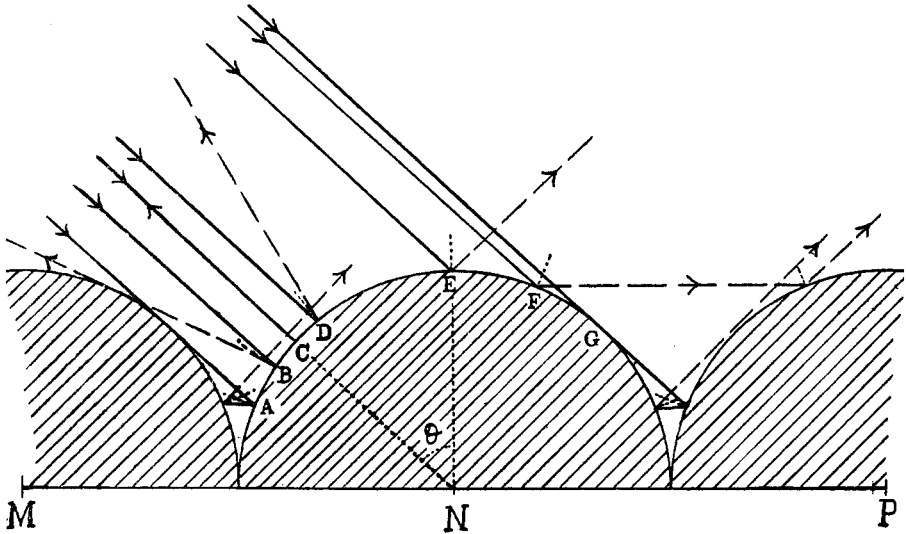


Fig. 3.—A diagram illustrating how translational motion becomes changed into vibrational motion by striking a rough surface.

of the velocity in the direction  $NP$  is diminished. Also for paths between  $D$  and  $E$ , as well as between  $F$  and  $G$ , the component of the velocity in the direction  $NP$  will be diminished. Only between  $E$  and  $F$  is the component in the direction of flow greater after collision than before. But the distance  $EF$  becomes zero when  $\theta = 90^\circ$  and it has its maximum value when  $\theta = 0^\circ$ , *i. e.*, when the translational motion is zero. Since all of the paths between  $A$  and  $G$  are equally likely, it follows that for this section at least, the average translational velocity of the small particles is diminished by collision irrespective of the size of the angle or of the velocity of the particle, and it can be easily shown that the same is true even if the particle is of considerable size. The same must be true *a fortiori* for sections other than the one passing through the centers of the spheres, for then there must, after collision, be a component velocity at right angles to the plane of the paper and therefore to the direction of flow. The section would be similar to the one given except that the circles would not touch, the spaces between them corresponding to the pores in which the translational velocity is quite certainly changed to disordered motion.

It follows as a corollary to the above theorem that a fluid made up of elastic particles which is in contact with a rough surface, tends to have a translational velocity identical with that of the surface. Thus the theorem explains how the molecules receive a velocity as they strike the surface *A* in Fig. 2 and also how that translational velocity becomes transformed into vibrational velocity at the surface *B*. If the motion of *A* were suddenly stopped, it follows that all of the flow must cease in a time which, for gases with particles having a velocity expressed in kilometers per second, must be inappreciable. It is to be particularly noted that collisions between molecules of a gas are not necessary for this type of viscous resistance. This resistance to flow is caused solely by the diffusion of the molecules, and we shall refer to this type of viscous resistance as "diffusional viscosity."

### The Viscosity of a Rarefied Gas and Slipping.

Further it is important to observe that for the case under consideration where the molecular mean free path is large in comparison with the distance between the surfaces *A* and *B*, the viscous resistance must be directly proportional to the number of molecules striking a unit area of the surface in a unit of time. *The viscous resistance of a rarefied gas is therefore directly proportional to the density, i. e., it is directly proportional to the pressure and inversely proportional to the volume, provided that the temperature and the mass of the molecules remain constant.* This is quite different from the law of Maxwell for gases at ordinary pressures. Such a falling off of the viscous resistance at very low pressure has actually been observed by Kundt and Warburg,<sup>1</sup> but they attributed it to slipping.<sup>2</sup> Meyer<sup>3</sup> has pointed out that this so-called "slipping" is directly proportional

<sup>1</sup> *Ann. Physik und Chem.*, **156**, 177 (1875).

<sup>2</sup> By the term "slipping," one refers to the movement of the layer of liquid which is in immediate contact with the boundary, over which the viscous flow is taking place. Ordinarily it is assumed that this layer of the fluid is stationary in respect to the boundary and therefore the slipping is zero. But an active discussion of slipping was started when Helmholtz and Piotrowski (*Wien. Ber.*, **40** (2a) 607 (1868)) announced that they had found a very perceptible amount of slipping by vibrating a hollow, polished metal sphere, which was filled with liquid and suspended bifilarly. However, the work of Poiseuille (*Mem. présent. par divers savants à l' academie Roy. des Science de l' Inst. de France*, **9**, 333 (1836)), Warburg (*Pogg. Ann.*, **140**, 367 (1870)), Wetham (*Proc. Roy. Soc.*, **48**, 225 (1890)), Couette (*Ann. chim. phys.*, [6] **21**, 433 (1890)), and Ladenburg (*Ann. Phys.*, [4] **27**, 157 (1908)) seems to prove that slipping never occurs between a liquid and a solid and regardless of whether the liquid wets the solid or not. Ladenburg repeated the work of Helmholtz and Piotrowski and found that they had overlooked a point in the theory so that even in their experiments he thinks that the slipping is negligible. Similarly it is admitted that slipping does not occur in gases at ordinary pressures. It is therefore at last only at pressures of a millimeter of mercury or less that slipping is still resorted to in order to explain the facts of experiment.

<sup>3</sup> Kinetic theory of gases.



to the free-path which is inversely proportional to the density. Hence the observed results are exactly in accord with the above law and we do not see that there is any evidence for any slipping at all.

The effect of temperature upon the viscosity of a rarefied gas may now be deduced. The velocity of the molecules is proportional to the square root of the absolute temperature, but if a molecule loses its translational velocity when it collides with the surface  $B$  and similarly receives the translational velocity of the moving surface when it collides with  $A$ , then the absolute amount of the vibrational velocity of the molecules will not effect the transfer of translational momentum at any given collision, except as it will affect the number of these collisions in proportion to this velocity. Hence, *the viscosity of a rarefied gas, at constant volume, varies directly as the square root of the absolute temperature, provided that the particles of the gas remain of uniform size. If, on the other hand, the pressure is kept constant, the viscous resistance must vary inversely as the square root of the absolute temperature.* We are not aware that there are at present any experimental facts to justify this conclusion which is so contrary to the behavior of gases at ordinary pressures, where the viscous resistance is directly proportional to some power of the absolute temperatures. The validity of this law depends upon the assumption that a molecule on collision assumes the translational velocity of the surface. Any other assumption would require "slipping" to occur, hence the testing out of the above law ought to afford valuable evidence upon the relative roughness or smoothness of different surfaces.

A change in the mass of the molecules of the gas has an effect upon the viscous resistance. At a given temperature and pressure the kinetic theory requires that the velocity is inversely proportional to the square root of the mass. The effect of an increase in the mass will be to increase the transfer of momentum in proportion to the mass, but the decrease in velocity will also decrease the viscous resistance inversely in proportion to the square root of the mass. Therefore, *the viscous resistance of a rarefied gas, at a constant temperature and pressure, is directly proportional to the square root of the molecular weight, but is independent of the other physical or chemical properties.*

The viscous resistance of a rarefied gas may be calculated as follows: Let  $u$  be the translational velocity of the surface  $A$  in respect to the surface  $B$ , the distance between them being  $s$ , and let  $N$  be the number of molecules per cubic centimeter, whose molecular weight is  $M$ , the density of the gas being  $\rho$ ; and let the average velocity of the molecules be  $U$ . The momentum removed from  $A$  at each collision is  $Mu$ . The number of molecules in a column of unit cross-section from  $A$  to  $B$  is  $Ns$  and they will reach the surface  $A$  at the average rate of  $U/6s$ , hence the total force per square centimeter required to maintain the motion of  $A$  is

$$\text{MuNu}/6 = \text{Uu}/6\rho$$

The viscosity, which is the force required when  $u = 1$  and  $s = 1$ , is therefore

$$\eta = \rho U/6s \quad (7)$$

which may be put into the form

$$\eta = \frac{Kp\sqrt{T}}{Sv\sqrt{M}}. \quad (8)$$

Where  $p$  is the pressure,  $v$  the volume,  $T$  the absolute temperature, and  $K$  a constant.

The most interesting and surprising thing about the above formula is its requirement that the viscosity of a rarefied gas must depend upon the dimensions of the apparatus used, the viscous resistance increasing as the space between the two surfaces is reduced.

#### Collisional Viscosity.

For the opposite extreme, we may conceive of a very viscous liquid, two layers of which,  $C$  and  $D$ , are shown in Fig. 4. The appearance is the

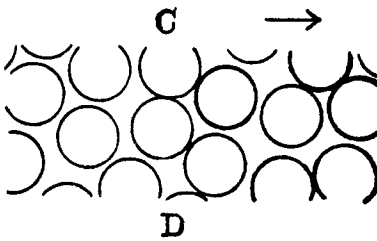


Fig. 4.

same as if a small portion taken from Fig. 2 had been greatly magnified, so that the molecules appear as disks instead of points, except that the molecular concentration is greatly increased. The effect of this increased concentration is to indefinitely decrease the molecular mean free path, so that the diffusional viscous resistance is negligible, but the actual

volumes of the molecules are comparable with the spaces which they occupy and collisions are immensely more frequent.

Since the layer  $C$  is nearer the surface  $A$  (not shown) than is  $D$ , it must move more rapidly than the layer  $D$ , according to the fundamental law of viscous flow discovered by Newton. The molecules of this layer must therefore overtake the molecules of  $D$  and in colliding with them tend to impart translational motion. Thus momentum passes through successive layers from  $A$  to  $B$ , and if  $B$  is free to move, it will take up the same velocity as  $A$ , all of the molecules taking part in the translational drift toward the right. But the surface  $B$  is assumed to be at rest, hence the layer  $C$  must have a velocity toward the right which is permanently higher than that of  $D$  by a fixed amount and the molecules of  $C$  must continue to overtake the molecules of  $D$  and in so doing to impart momentum to them. But in collisions between the molecules of one layer with the molecules of another layer, we have already shown in connection with Fig. 3 that translational motion is continually being transformed into disordered motion. Hence we have here a true model of viscous flow, in which translational

motion is continually being transformed into heat. In the extreme case, the effect of diffusion may be neglected, the viscous resistance being due solely to the collisions produced by the molecules of one layer overtaking those of another layer of smaller translational velocity. We shall refer to this as "collisional viscosity."

From the model described above we believe that it is possible to deduce the effects of changes in concentration, pressure, temperature, and size of the molecules upon this type of viscous resistance. Without attempting an elaborate proof at this time, it is probably clear that the number of collisions of the particles of one layer with those of another layer, due to their difference in translational velocity, will be directly proportional to the number of particles in each layer, *i. e.*, to the concentration. It will also be directly proportional to the rate of shear between the layers. Temperature and pressure can effect this resistance as they affect the concentration, but not otherwise. An increase in the temperature increases the vibratory motion of the molecules but it evidently does not affect the rate at which the molecules of one layer overtake the molecules of an adjacent layer which is moving more slowly. Increasing the mass of the particles would increase the momentum of the particles and hence the viscous resistance, but we must remember that with the increase in mass there is generally an alteration in the volume. Now it is evident that the collisional viscous resistance depends both upon the actual volume of the particles and upon the volumes which these particles occupy. If the particles are to be thought of as points, there could be no collisions and therefore no collisional resistance to flow. On the other hand, if the volume of the particles themselves could be made exactly equal to the space which they occupy, collisions would be most rapid and the collisional resistance would be a maximum.

The fact that in unassociated liquids the fluidity is directly proportional to the free volume, as stated above, seems to indicate that collisional viscosity is almost entirely responsible for the viscosity phenomena in ordinary liquids. It is also clear why associated liquids are exceptional. The breaking down of association, as for example by heating, would certainly furnish cause for a change in the collisional resistance, since dissociation is usually accompanied by a change in volume, which may be either in the actual volume of the particles or in the space which they occupy or both.

#### **The Mixed Regime.**

It has been indicated that in rarefied gases viscous resistance is certainly diffusional and in very viscous liquids it is probably collisional. In gases at ordinary temperatures and pressures the viscous resistance to flow is evidently the sum of the diffusional and collisional resistances. The total viscous resistance  $\eta$  is in every case given by the equation

$$\eta = \eta_c + \eta_d. \quad (9)$$

In rarefied gases, the collisional resistance  $\eta_c$  is equal to zero and in very viscous liquids, the diffusional resistance may be negligible. In all other cases, the complete formula should be applied. The diffusional viscous resistance in this calculation does not follow the simple formula given for the model described above, in connection with Fig. 2, for the reason that the molecular mean free path affects the resistance in this case, since it affects the number of layers a molecule can pierce before it gives up its translational momentum. The diffusional viscous resistance is then proportional to the free path, which in turn is inversely proportional to the density. We found that in a rarefied gas the diffusional viscous resistance is directly proportional to the density, hence it comes about that in this case the diffusional resistance is independent of the pressure. This is the law of Maxwell, which may be formulated as follows:

$$\eta_d = 1/3 \rho L U (1 + \alpha t)^n$$

where  $\rho$  is the density,  $L$  is the molecular mean free path,  $t$  is the temperature Centigrade, and  $U$  is the mean velocity. But we have seen above that

$$\eta_c = c/v - w$$

hence

$$\eta = c/v - w + 1/3 \rho L U (1 + \alpha t)^n. \quad (10)$$

Since diffusional viscosity becomes important only when the volume is large, we may put  $v - w$  for  $1/\rho$ . We will introduce the absolute temperature  $T$ , and for a first approximation assume that the exponent of  $T$  is unity, *i. e.*,  $n = 1$ . This is the value deduced from the theory by Maxwell, but experimentally determined viscosities give a value which is less than unity. But this discrepancy may conceivably be due to the collisional viscous resistance having been left out of account. We thus obtain an equation containing only three constants, which may be written in the form

$$\varphi = \frac{v - w}{A + BT(v - w)}. \quad (11)$$

This equation is very simple and convenient to apply. The following table serves to show to what extent it may be relied upon to reproduce the values obtained for carbon dioxide in both the liquid and gaseous states.

The deviations between the observed and calculated values are greatest in the critical zone where the experimental difficulties are the greatest. However, it cannot be affirmed that the agreement is within the experimental error, for apparently the deviation is systematic. But undoubtedly the agreement could have been improved by introducing another constant, as by giving the exponent of  $T$  in Formula (11) some other value than unity. It has seemed better to keep the formula in its simple form for the present.

TABLE I.—THE FLUIDITY OF CARBON DIOXIDE AS CALCULATED BY MEANS OF THE FORMULA  $\varphi = (v-w)/[A + BT(v-w)]$  WHERE  $w = 0.841$ ,  $A = 0.0002578$ , AND  $B = 4998$ , COMPARED WITH THE VALUES OBSERVED BY PHILLIPS<sup>1</sup> AT VARIOUS TEMPERATURES AND PRESSURES.

Temp. Abs.	Press. in atm.	v.	$\varphi$ obs.	$\varphi$ calc.	% Difference.
293	83	1.198	1215	1152	—5
	72	1.232	1297	1241	—4
	59	1.302	1435	1418	—1
	56	5.263	5376	4890	—9
	50	6.897	5650	5299	—6
	40	10.00	6024	5734	—5
	20	27.78	6410	6421	0
	1	546.4	6757	6907	+2
303	110.5	1.258	1299	1300	0
	104	1.280	1364	1355	—1
	96	1.316	1443	1441	0
	90	1.346	1555	1512	—3
	82	1.397	1689	1519	—11
	80	1.416	1770	1668	—6
	76	1.471	1890	1784	—6
	74	1.506	2020	1855	—8
	73	1.531	2092	1906	—9
	72	1.575	2183	1992	—9
	70	3.484	4367	4021	—8
	60	5.650	5348	4887	—9
	40	10.87	5952	5654	—5
	20	28.25	6289	6086	—3
1	565.0	6536	6594	+1	
305	120	1.266	1269	1318	+4
	112	1.287	1350	1369	+1
	104	1.316	1439	1439	0
	93	1.372	1595	1568	—2
	87	1.429	1706	1693	—1
	84	1.466	1786	1771	—1
	80	1.527	1894	1894	0
	76	1.675	2232	2168	—3
	75	1.802	2463	2379	—3
	74	2.778	3937	3506	—8
	70	3.922	4673	4240	—9
	60	5.882	5348	4918	—8
	40	11.111	5714	5641	—1
	20	28.41	6173	6201	0
1	568.1	6452	6553	+2	
308	114.5	1.324	1443	1455	+1
	109	1.349	1515	1512	0
	96	1.437	1706	1706	0
	88	1.531	1957	1896	—3
	85	1.597	2193	2021	—8
	80	2.024	2770	2690	—3
	75	3.460	4219	3966	—6

<sup>1</sup> *Loc. cit.*

TABLE I (Continued).

Temp. Abs.	Press. in atm.	$v$ .	$\phi$ obs.	$\phi$ calc.	% Difference.
	70	4.405	4673	4425	—5
	60	6.135	5618	4943	—12
	40	11.765	5747	5642	—2
	20	28.74	6135	6135	0
	1	574.7	6410	6487	+1
313	112	1.431	1751	1686	—4
	108	1.466	1852	1759	—5
	100	1.572	2070	1965	—5
	94	1.718	2415	2221	—8
	85	2.597	3717	3302	—13
	80	3.436	4587	3920	—14
	70	4.902	5000	4553	—9
	60	6.536	5348	4964	—7
	40	12.05	5682	5585	—2
	23.8	24.51	5917	5987	+1
	1	578.0	6369	6385	0

### Summary and Conclusions.

1. Attention is called to the fact that the fluidity is proportional to the "free volume," as it is called by Batschinski, not only in pure liquids and mixtures but also in suspensions of solids in liquids.

2. Since the fluidity of a liquid is proportional to the free volume, an equation resembling that of van der Waals may be used to reproduce the fluidity data as a function of the temperature and pressure.

3. Such a modified van der Waals' equation breaks down utterly when applied to gases, where *a priori* it might be expected to apply best. This discrepancy is due to the advent of an additional cause of viscous resistance in gases which does not apply in very viscous liquids. Thus the fluidity of a gas is invariably smaller than would be expected from the modified van der Waals' equation.

4. Viscous resistance in gases originates largely in the diffusion of the material which carries with it translational motion, which, in turn, by collisions becomes transformed into disordered motion. This kind of resistance to motion is called "diffusional viscosity."

5. But in viscous liquids the resistance to flow caused by diffusion is quite negligible. The resistance is shown to be due to the collisions of molecules of one layer with those of an adjacent layer moving at a slightly lower velocity. This transfer of momentum without a transfer of matter is called "collisional viscosity."

6. The viscosity of a gas or liquid is, therefore, the sum of the diffusional and collisional viscosities. We thus obtain an approximate formula  $\phi = (v - w) / [A + BT(v - w)]$  which can be used to reproduce the observed fluidities of carbon dioxide with considerable fidelity.

7. Reasons are given for the belief that slipping does not occur even

in rarefied gases. The apparent viscosity of a gas as it becomes rarefied, decreases rapidly, which is entirely in accord with the theory.

8. In gases at ordinary temperatures and pressures, the fluidity decreases as the temperature is raised, but the fluidity is nearly independent of the pressure. Both facts indicate that diffusional viscosity is of preponderating importance in gases. There is indication (cf. Fig. 1) that at very low temperatures the fluidity of gases is by no means independent of the pressure, being inversely proportional to the pressure. It is also possible that at very high temperatures the fluidity will increase with the pressure. It appears that this last has not yet been observed, but should so paradoxical a fact be discovered it would seem to offer a striking confirmation of the views here outlined.

9. The fluidity of practically all liquids increases with the temperature and decreases with the pressure. Most liquids *expand* as they are heated or as the pressure is removed, hence we may attribute the increased fluidity to the decreased number of collisions. Sulfur and water are exceptional in their behavior, but this may be explained on the basis of association.

10. In nearly all liquids an increase in the molecular weight causes an increase in the temperature required to produce a given fluidity, and this increase in temperature is proportional to the increase in molecular weight, in a given homologous series. There are exceptions to this generalization, such as formic and acetic acids, but the exceptions are more apparent than real, since, if we assume it to be strictly true and then calculate the association of these and other associated substances, we obtain values which are in satisfactory accord with the values given by other methods.

11. These deductions from the kinetic theory can be extended to solids and an explanation obtained for various phenomena. The more nearly perfectly elastic a substance is, the more nearly will it come back to its original position after being strained. Movement in a perfectly elastic solid is therefore explained by the molecules of one layer, as *C* in Fig. 4, moving up to those of another layer *D*, but not passing them in a single instance. Hence all of the energy is spent in producing a strictly limited amount of translational motion—the elastic limit. The energy exists as strain and as soon as the stress is removed, all of the work done is recovered, so that the process is reversible.

12. When ordinary imperfectly elastic solids are subjected to stress, work is done which only partly appears as strain, a part being transformed into heat. Finally, when the stress is removed the body does not come back at once to its former position. It comes back part way and then creeps slowly toward its old position. This is the much-discussed “elastic after-effect.” These phenomena may be explained as follows: When the body is subjected to stress a few of the molecules move over each other but the stress is not great enough to overcome the strains throughout the

mass and cause general flow or rupture. Wherever the molecules flow over each other heat is developed as in any viscous flow. When the stress is removed the strain tends to become immediately removed, but wherever the molecules moved over one another, the removal of the strain is hindered, the last of the strain disappearing through viscous flow under a constantly diminishing stress and therefore continuing through a long interval of time. This after-effect has been found<sup>1</sup> in undercooled liquids as well as solids.

13. Finally the after-effect is increased as the temperature is raised in ordinary solids and this may be explained by the expansion of the substance making it easier for the particles to move over each other in viscous flow, so that the fluidity of solids increases with the temperature as is true of most liquids. Guye and his co-workers<sup>2</sup> have assumed that because the vibrations in lead wires die down faster than in steel, the greater loss of energy in the former signifies that lead is more viscous than steel. Exactly the opposite conclusion seems preferable. Steel then is to be regarded as much more viscous than lead and for that very reason strains in steel are produced without nearly so much viscous flow as in lead or pitch.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

## IS THE DUHEM-MARGULES EQUATION DEPENDENT ON THE IDEAL GAS LAWS?

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In view of the importance of the Duhem-Margules equation in the theory of physical mixtures, no apology is necessary for raising the question as to whether it is a purely thermodynamic relationship, and therefore reliable under all circumstances, or requires modification in form as soon as vapors begin to deviate from the simple gas laws. That the latter is the case, would seem to be indicated by the fact that the gas laws are employed, at one stage or another, in every deduction of the equation that has been brought forward.<sup>3</sup> But closer study leads to the opposite conclusion: that the Duhem-Margules equation is absolutely general, that it must hold as true for all actual vapors, up to the critical points, as it would if the vapors behaved like ideal gases.

It is, of course, indifferent which form of thermodynamic procedure is

<sup>1</sup> Barus, *Am. J. Sci.*, [3] 45, 47 (1893).

<sup>2</sup> *Arch. sci. phys. nat.*, 26, 136, 263 (1906); 29, 49 (1909); 30, 133 (1910).

<sup>3</sup> Duhem, *Ann. de l'École normale sup.*, [3] 4, 9 (1887); Margules, *Sitzungsbericht der Wiener Akademie*, 104, II, 1243 (1895); Ostwald, *Lehrbuch der allgemeinen Chemie*, II, 2, pp. 636-640 (Ed. 2. Leipzig, 1902); Nernst, *Theoretische Chemie*, p. 115 (Ed. 7, Stuttgart, 1913).