

AN INVESTIGATION OF THE LAWS OF PLASTIC FLOW

By Eugene C. Bingham

CONTENTS

	Page
I. Introduction.....	309
II. Experimental.....	311
1. Description of apparatus.....	311
2. Experimental results.....	312
III. Types of viscous and plastic flow.....	319
Case 1. Viscous flow—Homogeneous fluids.....	319
Case 2. Viscosities additive—Emulsions.....	320
Case 3. Fluid mixtures—Fluidities additive.....	321
Case 4. Suspensions—The simplest case.....	326
Case 5. Seepage.....	326
Case 6. Nonplastic suspensions.....	327
Case 7. Plastic suspensions.....	329
IV. Discussion of experimental data.....	331
1. Law of pressures.....	331
2. Friction constant.....	335
3. Mobility.....	336
4. Slipping.....	340
V. Relation of results to earlier work on plasticity.....	341
VI. Models of plastic flow.....	351
VII. Summary.....	352

I. INTRODUCTION

Plastic flow is of importance in many diverse fields, such as geophysics, colloidal chemistry, metallurgy, ceramics, road building, and the lime and cement business. The property of plasticity, like ductility and malleability, is not at present strictly definable, although the term is much more familiar than the strictly defined terms "viscosity" and "fluidity."

In the study of plastic flow it has already been shown that most homogeneous solids will flow somewhat after the manner of liquids, if subjected to sufficient pressure. Copper, steel, lead, ice, menthol, glass, and asphalt fall in this class in so far as they may be regarded as homogeneous solids. But ordinarily plastic substances are not homogeneous solids but suspensions of finely divided solids in fluids, such as paint in oil, lime in water, and especially clay in water. Numerous papers have been devoted to the explanation of this latter type of plasticity.

Since glass and other similar bodies are often regarded not as solids but as very viscous liquids, the demarcation of viscous flow from plastic flow has not been sharply made. In fact, attempts have been made to give numerical values to the viscosity of ice, menthol, glass, and pitch, and Tammann¹ defines plasticity in a perfectly definite manner as the reciprocal of viscosity—in other words, plasticity and fluidity are synonymous.

Unfortunately, for the sake of simplicity, this definition is clearly untenable. If any finely divided solid, such as clay, be suspended in a liquid, the fluidity is lowered rapidly and in a perfectly linear manner, so that at a comparatively low concentration of clay the fluidity, as measured in the ordinary viscometer, approaches zero. Thus Durham and Bingham² found that a certain clay suspended in water gave a zero fluidity when the volume percentage had reached 6.95 (14.6 per cent by weight), this being independent of the temperature. This concentration apparently serves to sharply demarcate plastic from viscous flow. Suspensions more dilute than this critical concentration are subject to viscous flow, while those containing more solid in suspension are plastic.

These results are in harmony with the views of Maxwell,³ which are so important that we quote them at length:

If the form of the body is found to be permanently altered when the stress exceeds a *certain* value, the body is said to be soft or plastic and the state of the body when the alteration is just going to take place is called the limit of perfect elasticity. If the stress, when it is maintained constant, causes a strain or displacement in the body which increases continually with the time, the substance is said to be viscous. When this continuous alteration of form is only produced by stresses exceeding a certain value, the substance is called a solid, however soft it may be. When the very smallest stress, if continued long enough, will cause a constantly increasing change of form, the body must be regarded as a viscous fluid, however hard it may be.

Thus a tallow candle is much softer than a stick of sealing wax; but if the candle and the stick of sealing wax are laid horizontally between two supports, the sealing wax will in a few weeks in summer bend with its own weight, while the candle remains straight. The candle is therefore a soft (or plastic) solid, and the sealing wax a very viscous fluid.

What is required to alter the form of a soft solid is sufficient force, and this, when applied, produces its effect at once. In the case of a viscous fluid it is time which is required, and if enough time is given the very smallest force will produce a sensible effect, such as would be produced by a very large force if suddenly applied.

Thus a block of pitch may be so hard that you can not make a dint in it with your knuckles; and yet it will, in the course of time, flatten itself out by its own weight and glide down hill like a stream of water.

The italics and parenthesis are ours.

The experiments of Bingham and Durham² support the definition by Maxwell that a plastic body is one in which the form of

¹ Ann. der Phys., 7, p. 198; 1902.

² Am. Chem. Jour., 46, p. 278; 1911.

³ Theory of Heat.

the body is found to be permanently altered when the stress exceeds a certain value. These experiments indicate that the demarcation between the two régimes is very sharp, but they do not give any clue in regard to the laws of plastic flow, which must be known before a rational basis can be obtained for the quantitative measurement of plasticity.

II. EXPERIMENTAL

1. DESCRIPTION OF APPARATUS

The essential part of the apparatus used for the study of plastic flow is shown in Fig. 1. Pressure is admitted at *F* from an air reservoir connected with a water manometer. The chamber *D*, 2 cm² in diameter and 4.4 cm deep, contains the plastic substance to be forced through the glass capillary *A*, cemented into the brass cap *B*, this last being screwed tightly into the main part, using a lead gasket. The receiver *K* is held in place by a rubber collar *C* during the flow, but after the efflux the apparatus is removed from the constant-temperature bath in which it is immersed, the receiver closed with a rubber stopper, and weighed. At *M* there is a connection for rubber tubing leading out of the bath in order to keep the space in the receiver at atmospheric pressure.

On exposure to ordinary air the materials used were liable to changes in concentration due to evaporation, hence it was necessary to work in an atmosphere saturated with water vapor, using a chamber whose walls were kept moistened. The material was made up by weight in a glass-stoppered weighing bottle and then thoroughly shaken until the mass was uniform. Experiments were made to determine whether any change in the rate of flow would result from allowing the material to stand for several hours after being prepared, but no change was observed.

The possibility of the material changing its concentration on account of settling could only be counteracted by shaking the material in the apparatus immediately before a determination; but with materials which settle out rapidly, even

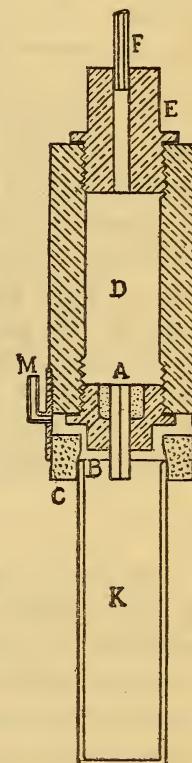


FIG. 1.—The viscometer used for very viscous or plastic materials

with this precaution, a difficulty arises from the solid material which packs into the mouth of the capillary. This difficulty was obviated by allowing a small amount of material to flow through the capillary into an extra receiver just before attaching the weighed receiver.

Since plastic materials take the temperature of the bath slowly, on account of the absence of convection currents, a considerable time was allowed for the equilibrium to be reached. Most of the experiments were carried out at 25°C , which was as near as practicable to the room temperature.

To determine whether there was noticeable separation of the components in the process of flow the material which had passed through the capillary was evaporated to dryness and weighed, but the separation was only noticeable when the rate of flow was very small (cf. Table 15).

The principal material used for this investigation was English china clay from St. Austell, Cornwall, England. Nearly all of it passed through a 200-mesh sieve. It was then put through the air analyzer devised by Pearson and Sligh, of the Bureau of Standards (Technologic Paper No. 48), using a 0.001-inch nozzle and 45 g per square centimeter air pressure. As a result 92 per cent of the material was obtained as an impalpable powder, which under the microscope seemed to consist of particles, of fairly uniform size, being rounded in shape and, very roughly, 0.002 mm diameter. Perhaps 1 per cent of the particles had a diameter ranging as high as 0.005 mm.

2. EXPERIMENTAL RESULTS

The dimensions of the six capillaries used are given in Table 1. A Zeiss standard millimeter was calibrated against a known standard belonging to the Bureau of Standards. The Zeiss standard millimeter was used to calibrate the Zeiss micrometer eyepiece No. 723. The ends of the capillaries were ground to a plane surface so that it was easy to obtain a good setting. The values given are in all cases the average of several readings. From these values the average radius, given in the next to the last column, was calculated by the known formulas.

TABLE 1
Dimensions of Capillaries Used

No.	The values of the radius in centimeters at the two ends (L and R) in the major and minor axes					
	L major	L minor	R major	R minor	Average radius ^a in centimeter at 20°	Length in centimeters at 20°
1	0.02974	0.02736	0.02965	0.02736	0.02848	2.468
2	.02977	.02714	.02974	.02707	.02846	1.2195
3	.02953	.02701	.02949	.02721	.02826	4.412
6.1	.06054	.05574	.05954	.05590	.05785	5.011
6.2	.06020	.05609	.06057	.05593	.05811	2.509
6.3	.06175	.05631	.06090	.05563	.05850	9.998

^a Average radius calculated according to formula, cf. Zeitschr. f. physik. Chem., 80 p. 683; 1912.

In the following tables all of the measurements obtained are given, numbered in chronological order, but arranged here in the order of increasing pressure. In the second column is given the time, t , of outflow in seconds, in the third column the pressure, P , in grams per square centimeter, corrected, except for kinetic energy and the hydrostatic head within the instrument. The kinetic energy correction is given in the seventh column. Experiments were made to determine the value of the hydrostatic head by varying the amount of material within the instrument when the flow began. For since the materials used have infinite viscosity as ordinarily measured and because in the course of the flow the material does not preserve anything like a horizontal surface, it is not evident a priori what the correction in question should be; in fact, whether it should be positive or negative. Experiment, however, failed to give any clear indication, hence it seemed best to neglect this correction altogether for the present. This correction could have been made small by using only relatively large pressures, but in this preliminary research it seemed best to use a wide range of pressures in order to discover disturbing conditions and thereby the best conditions for future work.

The densities of the suspensions, ρ , were calculated from the density of water and the density of the clay, which was determined to be 2.613 at 25°C. To obtain this density a 50 ml flask was filled with clay and weighed. Carbon tetrachloride was added, heated to boiling until the air was expelled, cooled to 25°C, and weighed.

TABLE 2

Experiments with Capillary No. 1, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume ($\rho=1.443$, Using Pure Water; Friction Constant=78)

No.	t	P	Wt.	Vol. per sec. $\times 10^3$	$C(P-f)t \times 10^3$	$C'P/t \times 10^3$	μ^a
13	600.2	80.1	2.119	2.45	88	0	11.42
18	300.0	101.4	1.938	4.47	537	0	1.86
14	300.2	101.8	2.166	5.00	489	0	2.04
15	300.3	102.3	2.126	4.91	509	0	1.97
16	360.0	102.9	2.307	4.21	607	0	1.65
17	126.0	103.3	0.818	4.50	578	0	1.73
20	300.1	126.8	2.395	5.53	905	0	1.10
19	300.2	128.6	2.660	6.14	846	0	1.18
2	180.0	154.6	2.353	9.05	868	0	1.15
1	180.1	156.5	2.326	8.95	900	0	1.11
7	200.0	178.1	3.412	11.82	864	0	1.16
[3]	180.0	191.0	2.383	9.17	1264	0	0.79]
8	180.3	206.1	3.738	14.37	915	0	1.09
9	192.3	206.8	4.299	15.49	853	0	1.17
11	180.2	234.7	5.194	19.97	805	0	1.24
10	108.7	235.2	2.770	17.66	576	0	1.74
4	180.1	270.9	6.040	23.23	852	1	1.18
5	102.0	288.0	3.228	43.84	491	1	2.04
12	99.6	294.3	6.029	41.94	529	1	1.89
6	103.2	295.3	6.684	44.87	497	1	2.02

Average mobility for medium pressures, 1.17.

Average mobility deviation from mean, 0.04.

^a The definition of the "mobility," which we represent by μ , will appear later, cf. p. 336 et seq. The significance of the constants C and C' are also given on p. 336. The friction constant f is discussed on pp. 331 and 335.

TABLE 3

Experiments with Capillary No. 2, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume ($\rho=1.443$, Using Pure Water; Friction Constant=78)

No.	t	P	Wt.	Vol. per sec. $\times 10^3$	$C(P-f)t \times 10^3$	$C'P/t \times 10^3$	μ
29	2100.2	40.9	1.056	0.3	-----	-----	-----
36	780.0	41.8	3.055	2.71	-----	-----	-----
28	600.2	50.6	2.126	2.45	-----	-----	-----
27	399.0	70.0	2.410	4.18	-----	-----	-----
24	300.3	79.9	2.129	4.91	80	-----	-----
25	200.0	84.7	1.837	6.36	217	-----	-----
23	280.0	90.7	2.943	7.21	364	0	2.75
26	231.4	91.8	2.442	7.31	390	0	2.57
22	240.2	99.9	3.785	10.92	415	0	2.41
21	190.0	107.0	4.474	16.32	368	1	2.72
30	180.1	108.6	3.794	14.60	423	1	2.37
31	180.2	118.1	4.200	16.15	514	1	1.95
33	98.3	127.4	3.406	24.00	426	1	2.35
32	90.0	140.4	4.154	31.98	404	2	2.49
34	88.3	150.8	5.012	39.32	383	2	2.62
35	90.0	157.8	5.426	41.77	386	2	2.60

Average mobility for medium pressures, 2.48.

Average mobility deviation from mean, 0.17.

TABLE 4

Experiments with Capillary No. 3, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume ($\rho=1.443$, Using Pure Water; Friction Constant=78)

No.	t	P	Wt.	Vol. per sec. $\times 10^3$	$C(P-f)t \times 10^3$	$C'\rho/t \times 10^3$	μ
46	720.0	105.4	3.094	2.98	511	0	1.96
45	360.2	135.7	2.246	4.32	743	0	1.34
38	360.0	158.6	1.994	3.84	1168	0	.88
41	865.2	190.2	7.570	6.06	1020	0	.98
42	398.3	234.7	3.858	6.71	1298	0	.77
43	300.0	236.4	4.168	9.62	916	0	1.09
44	200.0	241.3	3.281	11.36	800	0	1.25
39	300.0	280.9	4.739	10.94	1031	0	.97
40	330.0	297.7	4.938	10.37	1178	0	.85

Average mobility for medium pressures, 1.02.

Average mobility deviation from mean, 0.16.

TABLE 5

Experiments with Capillary No. 6.1, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume ($\rho=1.443$, Using Pure Water; Friction Constant=78)

No.	t	P	Wt.	Vol. per sec. $\times 10^3$	$C(P-f)t \times 10^3$	$C'\rho/t \times 10^3$	μ
60	180.2	99.6	4.764	18.32	1012	0	0.99
61	180.3	100.3	4.698	18.05	1088	0	.92
47	180.1	119.5	5.566	21.41	1668	0	.60
53	90.0	149.2	5.502	42.36	1445	0	.69
54	120.2	150.6	7.180	41.38	1508	0	.66
48	129.6	154.4	5.192	27.76	2369	0	.42
51	77.4	171.6	9.038	80.85	996	1	1.00
52	87.6	172.3	9.943	78.67	1028	1	.97
58	80.4	174.6	7.826	67.44	1232	1	.81
57	106.0	175.0	8.591	36.07	2308	1	.43
56	156.5	194.7	15.473	68.56	1463	1	.68
55	106.5	199.3	13.896	90.34	1154	1	.87
50	88.0	208.4	8.772	69.07	1587	1	.63
49	20.0	211.3	2.383	82.52	1389	1	.72
[59]	48.0	236.0	15.258	220.2	617	3	1.63]
62	114.6	260.9	14.41	87.09	1807	1	.55

Average mobility, 0.73.

Average mobility deviation from mean, 0.16.

Bingham and Durham have found that acids and alkalies have very great effect upon the rate of flow of suspensions. To determine whether or not alkalies from the glass or carbonic acid from the air affects the constancy of these determinations, suspensions were made up in a one-tenth per cent solution of potassium carbonate.

TABLE 6

Experiments with Capillary No. 6.1, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume ($\rho=1.443$, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=59.5)

No.	t	P	Wt.	Vol. per sec. $\times 10^3$	C(P-f)t $\times 10^3$	C' $\rho/t \times 10^3$	μ
67	299.7	49.9	9.59	22.18
66	206.5	60.0	11.50	38.57
68	105.3	79.7	11.55	76.01	229	1	4.39
65	57.4	101.4	14.41	173.9	261	2	3.87
69	36.0	124.0	12.69	244.3	227	3	4.47
64	33.8	148.1	19.49	399.5	191	5	5.42
70	27.4	158.6	15.17	383.5	222	5	4.60
63	22.7	200.0	18.37	560.7	215	7	4.82

Average mobility for medium pressures, 4.60.

Average mobility deviation from mean, 0.35.

The mobility is much greater with a trace of alkali present. The effect is very marked even when shaking the material up with the solution, being evidently "thinner."

TABLE 7

Experiments with Capillary No. 6.3, at 25° C, with 50 Per Cent Clay by Weight or 27.6 Per Cent by Volume ($\rho=1.443$, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=59.5)

No.	t	P	Wt.	Vol. per sec. $\times 10^3$	C(P-f)t $\times 10^3$	C' $\rho/t \times 10^3$	μ
83	270.9	88.8	16.28	41.5	253	0	3.96
71	120.2	117.4	13.45	77.5	337	1	2.98
72	88.9	147.6	14.20	110.8	358	1	2.80
79	78.2	163.8	15.91	141.0	334	1	3.01
76	60.6	175.3	14.87	170.0	307	1	3.27
81	48.7	185.7	16.74	238.2	239	1	4.21
75	51.2	195.6	15.23	206.1	298	1	3.37
74	44.9	197.1	17.26	266.3	233	2	4.32
73	41.0	198.2	16.76	283.2	221	2	4.57
80	37.3	211.7	16.34	303.5	226	2	4.46
77	32.8	238.7	16.06	339.5	238	2	4.24
78	23.3	262.1	15.77	468.8	195	3	5.21
82	22.4	264.4	13.88	429.2	215	3	4.71

Average mobility for medium pressures, 3.37.

Average mobility deviation from mean, 0.41.

These values are irregular, but particularly at the higher pressures.

TABLE 8

Experiments with Capillary No. 6.2, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume ($\rho=1.443$, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=59.5)

No.	t	P	Wt.	Vol. per sec. $\times 10^3$	$C(P-f)t \times 10^3$	$C'\rho/t \times 10^3$	μ
88	190.7	33.5	12.10
87	73.5	50.4	17.54
86	55.9	59.9	14.20
85	30.4	68.5	10.63	242	63	6	17.7
84	24.8	80.2	10.32	288	125	7	8.47
89	16.8	117.0	14.20	585	172	15	6.38

Average mobility for medium pressures, 7.42.

Average mobility deviation from mean, 1.04.

TABLE 9

Experiments with Capillary No. 6.2, at 25° C, with 60 Per Cent Clay by Weight or 36.40 Per Cent by Volume ($\rho=1.585$, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=119)

No.	t	P	Wt.	Vol. per sec. $\times 10^3$	$C(P-f)t \times 10^3$	$C'\rho/t \times 10^3$	μ
100	180.2	118.3	3.378	11.8
96	400.0	136.8	5.245	8.3
94	299.7	155.3	4.223	8.9	7131	0	0.140
95	245.1	174.1	4.993	12.8	7495	0	.133
93	180.2	200.2	4.848	17.0	8368	0	.120
92	182.1	234.5	7.128	24.7	8184	1	.122
91	209.8	263.8	10.03	30.2	8398	1	.119
98	180.2	268.8	9.236	32.3	8101	1	.124
97	190.1	296.3	8.271	27.45	11298	1	.088
99	132.6	298.4	7.374	35.1	8945	1	.112

Average mobility for medium pressures, 0.119.

Average mobility deviation from mean, 0.10.

TABLE 10

Experiments with Capillary No. 6.2, at 25° C, with 70 Per Cent Clay by Weight or 47.10 Per Cent by Volume ($\rho=1.758$, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=?)

No.	t	P	Wt.
102	2730	272.6	0.794
101	670	302.0	.738

The viscosity of a suspension consisting of 25 per cent clay by weight or 11.28 per cent by volume, $\rho=1.179$, using 0.1 per cent of potassium carbonate was determined in a horizontal tube viscometer to be 0.0190, at 25° C, which corresponds to a fluidity of 52.7.

TABLE 11

Experiment with Capillary No. 1, at 25° C, with 47 Per Cent Clay by Weight or 25.28 Per Cent by Volume ($\rho=1.405$, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=40)

No.	t	P	Wt.	Vol. per sec. $\times 10^3$	$C(P-f)t \times 10^3$	$C'\rho/t \times 10^3$	μ
112	229.8	43.3	5.114
111	200.0	57.7	3.682	13.1	138	0	7.24
110	179.8	70.3	6.052	23.9	130	1	7.73
113	150.0	94.1	8.321	39.5	141	1	7.11
105	139.8	95.2	9.144	46.5	122	1	8.30
106	73.9	142.4	7.883	75.9	138	2	7.33
107	86.0	199.5	14.80	122.0	134	3	7.64
109	59.8	230.1	13.74	163.5	119	4	6.12
108	63.6	248.0	17.26	193.1	111	5	9.48

Average mobility for medium pressures, 7.35.

Average mobility deviation from mean, 0.46.

TABLE 12

Experiments with Capillary No. 1, at 40° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume ($\rho=1.438$, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=59.5)

No.	t	P	Wt.	Vol. per sec. $\times 10^3$	$C(P-f)t \times 10^3$	$C'\rho/t \times 10^3$	μ
114	240.0	106.8	11.69	33.8	143	2	7.08
115	119.4	148.0	12.78	75.6	122	5	8.54
116	112.2	202.1	15.73	97.4	150	6	6.95
119	102.5	207.9	15.40	104.4	146	7	7.19
117	66.0	247.8	14.94	157.3	123	10	8.89
118	50.1	280.4	12.81	177.8	128	12	8.63

Average mobility, 7.88.

Average mobility deviation from mean, 0.81.

TABLE 13

Experiments with Capillary No. 1, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume ($\rho=1.443$, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=59.5)

No.	t	P	Wt.	Vol. per sec. $\times 10^3$	$C(P-f)t \times 10^3$	$C'\rho/t \times 10^3$	μ
125	309.7	89.62	9.932	22.2	139	1	7.22
124	259.4	127.6	13.75	36.7	190	1	5.28
120	241.6	156.0	17.27	49.8	199	1	5.06
126	171.2	170.9	14.13	57.2	200	2	5.04
127	147.8	188.5	14.20	66.6	199	2	5.07
121	132.3	202.3	16.62	87.0	168	2	6.02
123	84.8	249.0	14.22	116.1	167	3	6.08
122	78.6	287.2	14.84	130.8	168	3	6.05

Average mobility for medium pressures, 5.11.

Average mobility deviation from mean, 0.08.

III. TYPES OF VISCous AND PLASTIC FLOW

CASE I. VISCOUS FLOW—HOMOGENEOUS FLUIDS.—If two horizontal planes at unit distance apart are acted upon in opposite directions by a unit tangential force per unit area, the velocity of one plane in respect to the other is a measure of the fluidity of the substance filling the space between the planes. Viscosity (η) is the reciprocal of the fluidity (φ). In general, if dr is the distance between two planes acted upon by the tangential force P , the displacement produced per unit of time is

$$dv = \varphi P dr \dots \dots \dots \quad (1)$$

In order to deduce a formula which will permit of the experimental determination of viscosity, several assumptions must be made; they are as follows:

1. It is generally assumed that where two substances, or two phases of the same substance, come in contact, the velocity of both is identical at their surface of separation, i. e., there is no "slipping."
2. Each stratum of the fluid must move solely in the direction of the shearing force, i. e., there must be *stream line motion* only. Otherwise a correction must be made for the kinetic energy improperly lost.
3. It is assumed that the resistance to flow varies directly as the rate of shear, and becomes zero when the shear is zero.
4. It is further assumed that the resistance is directly proportional to the area of surface, but independent of the curvature of the surface.

With these assumptions the viscosity formula for a straight capillary tube, squarely cut off at the ends and having a bore which is a true circular cylinder, is

$$\eta = \frac{\pi g r^4 P t}{8 V(l + \lambda)} - \frac{m \rho V}{8 \pi t(l + \lambda)} \dots \dots \dots \quad (1a)$$

where V is the volume of flow in cubic centimeters, l the length, and r the radius of the capillary in centimeters, t the time in seconds, P the average difference in pressure in grams per square centimeter at the two ends of the capillary, g is the gravity constant, m is a constant equal to 1.12 according to Boussinesq,⁴ λ is a correction to be made to the length of the capillary because of the stream line motion not becoming established at the entrance

⁴ Compt. rend., 110, pp. 1160, 1238 (1890); 113, pp. 9, 49 (1891).

and is negligible when the length of the capillary is many times the diameter. This formula gives the viscosity (η) in c. g. s. units.

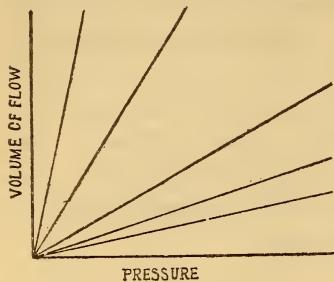


FIG. 2.—Typical diagram of viscous flow. This is in marked contrast with the diagrams of plastic flow, Figs. 8 and 9.

It is thus a fundamental characteristic of viscous flow that, so long as the pressure is small, the volume of the flow varies directly as the pressure. Or expressed graphically, the volume of flow plotted against the pressure will give a family of straight lines proceeding from the origin, Fig. 2, irrespective of the substance or the method of measurement.

CASE 2. VISCOSITIES ADDITIVE—EMULSIONS.—If the fluid is not identical throughout, the viscosity may yet be calculated in special cases. Take first the case of a series of vertical lamellae arranged alternately, as in Fig. 3, and subjected to a horizontal shearing stress. For convenience suppose that the lamellae of the one substance *A* all have the same thickness s_1 and that the lamellae of the substance *B* have the uniform thickness s_2 , etc.

Let the viscosities of the substances be η_1, η_2, \dots and the shearing forces per unit area p_1, p_2, \dots respectively, then if R is the distance between the horizontal planes, the velocity of the moving surface is

$$v = \frac{R P}{H} = \frac{R p_1}{\eta_1} = \frac{R p_2}{\eta_2}$$

where H is the viscosity of the mixture, and P is the average shearing force over the whole distance S . But

$$P S = p_1 s_1 + p_2 s_2 + \dots$$

hence

$$H = \frac{R(p_1 s_1 + p_2 s_2 + \dots)}{S}$$

But since $\frac{s_1}{S}$ is the fraction by volume of the substance *A* present in the mixture which we may designate a , and similarly $s_2/S = b$, etc.,

$$H = a\eta_1 + b\eta_2 + \dots \quad \dots \quad (2)$$

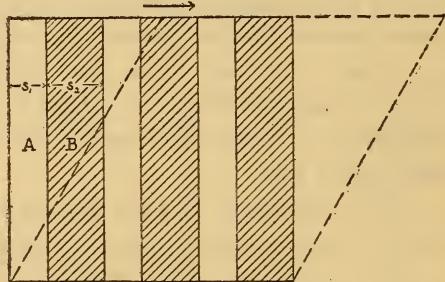


FIG. 3.—Additive viscosities

This case is of particular interest in connection with emulsions. The formula tells us that the viscosity of the mixture is the sum of the partial viscosities of the components, provided that the drops of the emulsion completely fill the capillary space through which the flow is taking place.

CASE 3. FLUID MIXTURES—FLUIDITIES ADDITIVE.—If the lamellae are arranged parallel to the direction of shear, as shown in Fig. 4, we have a constant shearing stress, so that

where v_1, v_2, \dots are the partial velocities as indicated in the figure.

There are two different ways of defining the viscosity of a mixture, and it becomes necessary for us to adopt one of these before we proceed:

i. If we measure viscosity with a viscometer of the Coulomb, or disk, type, we actually measure the velocity v , BS in the figure, and we very naturally assume that

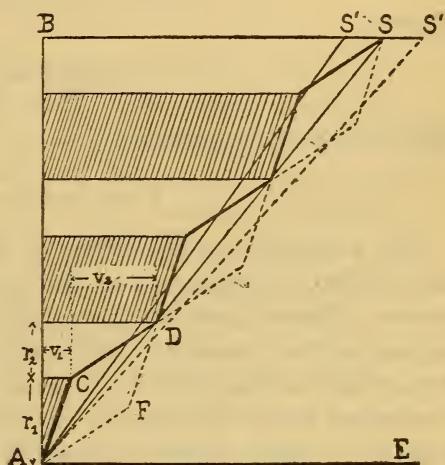


FIG. 4.—*Additive fluidities*

$$P = \frac{H}{R} v \quad \dots \dots \dots \quad (3a)$$

2. It is more usual, however, to calculate the viscosity from the volume of flow, as in the Poiseuille type of instrument. Let v' , BS' in the figure, be the effective velocity which the surface BS would have, were the series of lamellae replaced by a homogeneous fluid having the same volume of flow. The effective velocity is related to the quantity of fluid U passing per second in a stream of unit width, as follows:

$$U = \frac{v' R}{2}$$

Let the viscosity as calculated from the flow, as for a homogeneous fluid, be H' , then

$$P = \frac{H'v'}{R} = \frac{2}{R^2} H' U \quad \dots \dots \dots \quad (3b)$$

It is to be noted that had the less viscous substance been in contact with the surface AE , the effective velocity of flow would have been represented by the distance BS'' . We shall take the former of these for our definition of the viscosity of a mixture, since, as we shall now show, by using it the viscosity is independent of the number or the arrangement of the lamellae.

Since

$$v = v_1 + v_2 + \dots$$

we obtain from equations (3) and (3a) that

$$PR\Phi = P(r_1\varphi_1 + r_2\varphi_2 + \dots)$$

or since

$$a = \frac{r_1}{R}, \ b = \frac{r_2}{R}, \text{ etc.}$$

the fluidity of the mixture is

The fluidities are, according to this definition, strictly additive and entirely independent of the number and arrangement of the layers. Since, however, the viscosities are usually calculated by means of the Poiseuille formula based on the volume of flow, it is important to determine for a given arrangement of lamellæ what correction must be made to the effective viscosity, as calculated from the volume of flow, to make it accord with the true viscosity, as defined above and as obtained by the disk or other similar method for the measurement of viscosity.

Reverting again to the figure, we find that

$$U = \frac{v_1 r_1}{2} + v_1 r_2 + \frac{v_2 r_2}{2} + v_1 r_1 + v_2 r_1 + \frac{v_1 r_1}{2}$$

If there are n pairs of alternate lamellæ of the two substances A and B

$$U = \frac{1}{2} \left[n^2 v_1 r_1 + n(n+1) v_1 r_2 + n^2 v_2 r_2 + n(n-1) v_2 r_1 \right] \dots \dots \dots (5)$$

Since $n = \frac{R}{r_1 + r_2}$, on substituting into equation (5) the values of

v_1 and v_2 , we get

$$U = \frac{R^2}{2} P \left[a\varphi_1 + b\varphi_2 + \frac{ab}{n} (\varphi_1 - \varphi_2) \right]$$

and if $\Phi' = \frac{I}{H'}$ we obtain from equation (3b)

$$\Phi' = a\varphi_1 + b\varphi_2 + \frac{ab}{n} (\varphi_1 - \varphi_2) \dots \dots \dots \quad (6)^a$$

and when $n = \infty$, the fluidity becomes simply

$$= a\varphi_1 + b\varphi_2$$

and in this case

$$\Phi' = \Phi \dots \dots \dots \quad (7)$$

In a homogeneous mixture it appears, therefore, that the two definitions lead to the same fluidity, and experimental results lead us to believe that this is the case usually presented in liquid mixtures, since the disk method and the capillary tube method give the same fluidity. If, however, the number of lamellæ is small, as may well be the case in very imperfect mixtures, or when the flow takes place through very narrow passages, the effective fluidity as calculated from the volume of flow may be either greater or less than the sum of the partial fluidities of the components, depending upon the order of the arrangement of the lamellæ in reference to the stationary surface. The amount to be added or subtracted from the effective fluidity in order to obtain the true

fluidity is represented by the term $\frac{ab}{n} (\varphi_2 - \varphi_1)$, corresponding to the areas ACD , etc., or AFD , etc., Fig. 4.

A combination of the cases 2 and 3 would lead to a checkerboard arrangement, but it may now be shown that such an arrangement tends to reduce to the case where the fluidities are additive.

If the arrangement considered in Fig. 3 is subjected to continued stress, the lamellæ will tend to become indefinitely elongated as indicated in Fig. 5; and unless the surface tension intervenes, as may be the case in immiscible liquids, the lamellæ will approach more and more nearly the horizontal position. Thus, so far as we

^a Dr. E. Buckingham of the Bureau of Standards has checked this derivation by another method. A more general solution has been furnished by Mr. C. A. Briggs of this Bureau.

Let N be the total number of layers. If there are m different liquids having fluidities $\varphi_1, \varphi_2, \varphi_3, \dots$ and the thicknesses of the layers of each liquid are r_1, r_2, r_3, \dots respectively, the layers being arranged in this order and repeated $\frac{N}{m}$ times, the fluidity will be

$$\Phi' = a\varphi_1 + b\varphi_2 + c\varphi_3 + \dots + \frac{m}{N} \left[a\varphi_1(b+c+d+\dots) + b\varphi_2(-a+c+d+\dots) + c\varphi_3(-a-b+d+e+\dots) + \dots \right]$$

can determine without solving the complicated problem of the molecular motions, it seems certain that the fluidities will become more and more nearly additive as the flow progresses and the mixture becomes more and more nearly complete. The results of experiment verify this conclusion wherever there is no evidence of chemical union between the components of the mixture.

It has been demonstrated⁵ that the viscosity of a given mixture must always be less when the fluidities are additive than when the viscosities are additive, hence the viscosity is greatest when the lamellæ are perpendicular to the direction of the shear; it is least when the lamellæ are arranged parallel to the direction of shear.

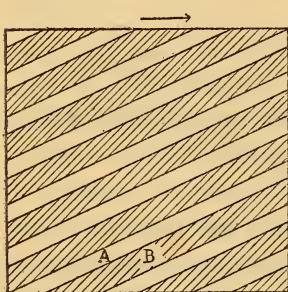


FIG. 5.—The arrangement shown in Fig. 3 after flow has taken place. Conditions are seen to approach those of Fig. 4, so that the fluidities of a mixture tend to become additive

But the "effective" viscosity may be made still less by placing the more fluid substance in contact with the stationary surface and having the number of lamellæ as small as possible.

Scarpa⁶ has raised the important question, If the fluidities of homogeneous mixtures are additive, should there not be a mechanical separation of the components of the mixture when it is simply forced through a narrow passage, such as has never been observed? It is clear that the flow of one component *A* will cause the component *B* to be carried along, even though the fluidity of the latter may be zero.

The total quantity of *A* flowing in a unit of time, regardless of whether it is derived from the fluidity of *A* or *B*, is made up of the terms of equation (5) containing r_1 , and is

$$U_1 = \frac{R^2 P}{2} \left(a^2 \varphi_1 + \frac{n-1}{n} ab \varphi_2 \right)$$

and similarly the rate of flow of the component *B* is

$$U_2 = \frac{R^2 P}{2} \left(b^2 \varphi_2 + \frac{n+1}{n} ab \varphi_1 \right)$$

When $n = \infty$

$$\frac{U_1}{U_2} = \frac{a}{b} \dots \dots \dots \quad (8)$$

which proves that when the number of lamellæ is large, the substance flows in exactly the ratio in which the components are present. In other words, there is no separation at all.

⁵ Phys. Review, 35, p. 411; 1922.

⁶ Rend. soc. chim. ital. II, 5, p. 363; 1913.

There will be a separation of the components of the mixture when the thickness of the lamellæ is great or when the passage through which the substance is forced is very small, for in either case n will be small. The separation may be calculated from the expression.

$$\frac{U_1}{U_2} = \frac{a}{b} \cdot \frac{na\varphi_1 + (n-1)b\varphi_2}{(n+1)a\varphi_1 + nb\varphi_2} \dots \dots \dots \quad (9)$$

If the two components have the same fluidity and are present in equal proportion, the component A will flow at only one-third of the rate of B when $n=1$. Even if the fluidity of B is zero, it will flow twice as rapidly as A , under the above conditions. Since this ratio is independent of the fluidity of A , it follows that the flow of B may be increased by making the fluidity of A large.

An ingenious application of the above principle was made by the Southern Pacific Railroad,⁷ when it was found that the pressure required to pump heavy oils through long pipe lines was inconveniently large. The problem was to get the maximum flow of oil for a given expenditure of work and with a given diameter of pipe. By using a rifled pipe and injecting about 10 per cent of water along with the oil, the water was thrown to the outside of the pipe by the centrifugal action caused by the rifling, and thus by a seeming paradox the water lubricated the oil, so that the delivery became from 8 to 10 times what would have been the case had the water not been added.

Similar experimental confirmation of the principle was obtained by the author as follows: Using capillary No. 1 in the viscometer we have employed above, it was found that 13 ml of pure water at 25° C under 60 g per square centimeter pressure would flow in 33 seconds. Pure cottonseed oil under the same conditions required 1640 seconds. A mixture was then made containing one-third oil and two-thirds water by volume. Had the water completely flowed through the capillary before the oil began to flow, the time of flow of the mixture should have been $22 + 547 = 569$ seconds; yet only 391 seconds were actually required, which is less than the time theoretically required for the flow of the oil alone. The difference of 178 seconds is due to the water forming a lubricating film for the oil as the water drained out of the viscometer. This effect may be regarded as a kind of "slipping."

⁷ Engineering Record, 57, p. 676; 1908.

It is possible that under special circumstances there may be a separation of the components of a mixture even when thoroughly mixed. This would manifest itself when the capillary passages approached molecular dimensions and there was a difference in the adhesion of the components of the mixture for the surface of the passages. The component with the least tendency to wet the walls would tend to be carried along. As a matter of fact Gilpin⁸ and his coworkers have found a separation of the components of petroleum in flowing through finely powdered materials.

CASE 4. SUSPENSIONS—THE SIMPLEST CASE.—The above cases apply primarily to pure homogeneous fluids, fluid mixtures, and emulsions. We come now to the consideration of suspensions of solids in fluids. In its simplest aspect we have but a limiting example of case 3, where the lamellæ of one component have zero fluidity. We have already seen that if the lamellæ were thin enough the suspension would flow without separation of the components. If $\varphi_2 = 0$, the fluidity Φ of the suspension is

$$\Phi = a\varphi_1 \dots \quad (10)$$

that is, the fluidity of the medium will be decreased in exactly the ratio which the volume of the solid bears to the total volume of the suspension.

If, however, the lamellæ of solid *B* have an irregular surface, this law will not hold. If, for example, the lamellæ are pierced by numerous fine pores, the fluid will fill these pores, yet the stream lines will neither pass through the pores or be appreciably distorted by their presence. The fluidity is then

$$\Phi = (a - d)\varphi_1$$

where *d* is the fraction of the total volume occupied by the pores.

CASE 5. SEEPAGE.—A solid stratum placed at right angles to the direction of shear prevents all viscous flow until the pressure becomes sufficient to produce rupture, as equation (2) requires. If this stratum is pierced by one or more cylindrical pores, flow will take place and for a given area of pores it is easy to calculate from equation (1a) that the rate of flow will vary directly as the square of the radius of the pores. This effect of the variation of the diameter of the pores upon the rate of flow is often

⁸ Am. Chem. J., 40, p. 495 (1908); 44, p. 251 (1910); 50, p. 59 (1913).

underestimated. If a single pore opening 1 cm in diameter in a plug be replaced by a multitude of pores with the same total area, but with a diameter of only 0.0001 cm, this being of the order of magnitude of the pores in the finest clay, then a pressure which would cause a flow of 1 cm³ in a minute through the large opening would, according to Poiseuille's law, require 12 years to force 1 cm³ of fluid through the small pores.

It is well known that compact clay is almost impervious to both water and oils, and therefore they are often associated, the clay forming an impervious stratum through which the water or oil does not penetrate. For this reason clay is used for the cores of dams in as compact a state as possible. The fineness of the pores has an important bearing upon the penetration, retention, and circulation of water in soils. It is well known to the chemist that the rapidity of filtration increases very rapidly with the increase in the size of the grain and consequently in the size of the pores.

The fact that jellies set so as to become apparently solid substances, when only a minute fraction of the total volume is made up of true solid, is doubtless due to the formation of a connected network, which prevents the viscous motion of the jelly as a whole, and the excessively fine pores prevent the appreciable flow of the medium. It is to be expected that diffusion and electrical conduction through such a substance would be practically unimpeded, and such is the case.

CASE 6. NONPLASTIC SUSPENSIONS.—A sphere suspended in a fluid of its own specific gravity, Fig. 6, is the simplest case of a suspension. The shearing of the fluid, which causes any cubical figure of the fluid to assume the form of a rhombohedron, will cause the sphere to rotate, greatly assisting the flow. The stream lines are curved on account of the presence of the sphere, but the sphere itself moves in a linear direction and with the velocity of the stratum of liquid which would, if continuous, pass through the

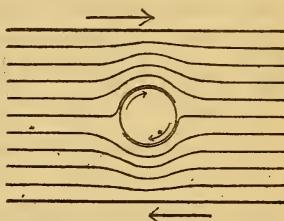


FIG. 6.—Showing the distortion of the stream lines by the presence of a solid sphere in viscous flow. If the sphere is situated midway between the upper and lower surfaces which are supposed to be sheared with equal velocity toward the right and left, respectively, it is evident that the sphere and the stratum which would pass through its center are not moving either to the right or to the left, i. e., they have the same velocity. The figure is evidently diagrammatic only

center of the sphere.⁹ Spheres in the same stratum do not tend to approach each other, since they all have the same velocity.

Spheres in different strata move with unequal velocities; hence collisions must take place, depending upon the radii of the spheres and their number per unit volume as well as upon the attraction or repulsion that may exist between them. The surfaces of two spheres which are approaching each other must be moving in opposite directions which are at right angles to the line joining their centers, Fig. 7a. The viscous resistance to this shearing action as

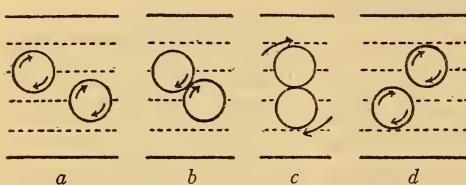


FIG. 7.—*Two spheres before, during, and after collision. The initial rotation of the individual spheres is lost on collision and this results in the dissipation of energy as heat. In the place of this individual rotation there develops a rotation of the system. It should be noted that this latter rotation causes the centers of the spheres to move in a transverse direction, indicated by the distances from the dotted lines*

they approach will rapidly dissipate as heat their energy of rotation.

The contact of two particles, which are large in comparison with molecular dimensions, brings the laws of ordinary friction into play. The spheres cannot rotate unless the torque exceeds a certain definite value, which depends upon the pressure existing normal to the surfaces at their point

of contact, and this pressure in turn depends not only upon the rate of shear but on the attraction or repulsion which may exist between the spheres.

When two spheres come into contact, Fig. 7b, they must remain in contact for a definite period. If the spheres were without

⁹ Einstein (*Ann. der Physik*, 19, p. 289, 1906) and Hatschek (*Kolloid-Zeitschrift*, 7, p. 301, 1910; 8, p. 34, 1911; *Trans. Faraday Society*, March, 1913) have both considered the case of suspensions of spherical particles at low concentrations. They both arrive at a formula

$$H = \eta_1 (1 + kb)$$

or

$$\Phi = \frac{\varphi_1}{1 + kb}$$

where b is the volume fraction of solid present and k is a constant for which Hatschek deduced the value of 4.5 and Einstein of 1. The formula is hyperbolic in form, while the formula, equation (12), obtained by Bingham and Durham experimentally, and confirmed by the experiments of Oden (*Zeitschr. f. physik. Chem.*, 80, p. 709, 1912) is linear.

There is a slip in Hatschek's reasoning. He says: "It is obvious that the liquid at the upper pole of each spherical particle moves with a somewhat greater velocity than at the lower pole, which is equivalent to a translatory movement of the particles with a velocity equal to half the difference of the two velocities prevailing at the two poles." He thus neglects entirely the rotation of the spheres and assumes that they are moving faster than the stratum of fluid which would pass through the centers of the spheres. That these two motions are equivalent is at least not self-evident. His formula is obtained by the employment of Stokes's formula for a sphere moving through a viscous medium without rotation.

It is worth noting that if their formula held at high concentrations the pure solid would have a fluidity of 18 per cent (Hatschek) to 50 per cent (Einstein) of the fluidity of the continuous medium, irrespective of the nature of the medium. This result is of course absurd. We believe that it shows that the values obtained by the use of the formula will always tend to be higher than the values found experimentally.

attraction or repulsion for each other, they would become separated as soon as their centers had come to be in the same vertical plane, Fig. 7c.

The spheres cannot rotate as individuals unless the torque exceeds a certain minimum value, which depends upon the pressure which exists normal to the surfaces in contact. Seepage can take place at low rates of shear, but we are here considering the flow of the mass.

During the time of contact of two spheres they rotate as a whole and pass out of the strata of liquid to which they formerly belonged, Fig. 7c, and into strata of widely different velocities. During this period of acceleration the liquid will flow around the spheres and through the interstices between them. Thus, other spheres tend to collide with those already in contact, after which the combined mass tends to rotate as a whole. When equilibrium is reached these clots will have a certain average size, depending upon the number, size, and specific attraction of the particles.

For the present purpose, the important thing to observe is that as these clots increase in size and number there comes a point when the clots come in contact across the entire width of the passage. At this point viscous flow stops and plastic flow begins.

For a given substance and volume concentration, the number of collisions will be proportional to the number of particles which varies inversely as the cube of the radius. But if the angular velocity is independent of the radius, the energy of rotation will vary with the square of the radius, hence the loss of energy, due to collisions, will be inversely proportional to the radius.

Experiment proves that the viscous flow of suspensions follows the law^{9a}

$$\Phi = \left(1 - \frac{b}{c} \right) \varphi_1 \dots \dots \dots \quad (12)$$

where b is the concentration of solid by volume and c is the particular value of b at which the fluidity of the suspension becomes zero. The value of c can vary only from 0 to 1, the value increasing with the size of the particles. When $c = 1$ the formula becomes the same as in Case 5, $\Phi = a\phi_1$ where no collisions are taking place. This perhaps indicates that the decrease from unity in the value of c actually found is due solely to collisions.

CASE 7. PLASTIC SUSPENSIONS.—We have supposed that the stress is insufficient to overcome the friction between the particles.

^{9a} Phys. Review, 35, p. 423; 1912.

If the stress is sufficient to cause the surfaces to slip over each other, a flow will result which must be regarded as plastic in its nature, since a certain definite stress is required for its production. It is evident that the friction must increase as the number of continuous chains of particles across the passage is increased.

There is a superior limit to the volume concentration of solid in this type of plastic flow. If the solid phase is made up of spheres of equal size, no further concentration is possible after the spheres are closely packed. As soon as this becomes the case, movement among the particles is prevented and the only flow possible is by slipping at the boundary or at a surface of rupture, and of the medium filtering through the interstices. There are two methods of closely packing spheres, the tetrahedral packing with a pore

space of $1 - \frac{\pi}{3\sqrt{2}}$ or 25.96 per cent by volume and the cubical

packing with a pore space of $1 - \frac{\pi}{6}$ or 47.64 per cent by volume.

Since the pore space is independent of the radius of the particles, and since interlocking of the spheres occurs as soon as the pore space becomes less than 47.64 per cent, the concentration of solid corresponding to this pore space appears to be the maximum concentration for the occurrence of plastic flow of the first type, and at this concentration of 52.36 per cent slipping must take place if the mass is to flow as a whole.

While the maximum concentration for plastic flow is thus independent of the size of the particle, we have seen that the concentration at which plastic flow begins decreases with the decreasing radius of the particles. To have a considerable range of plasticity, the spheres must therefore be very small. It is this fact which is of fundamental importance in the study of plastic substances.

What has been stated above in regard to the effect of piercing the lamellae with fine pores may be extended to the case where the particles are porous spheres or bodies with reentrant angles or other irregular outline.

If the view here presented is correct, the point where plastic flow begins is independent of the viscosity of the medium, so long as the attraction or repulsion between the particles is the same. For example, in dry clay the medium filling the pores is air. When the clay, thoroughly worked to separate the particles from each other, is put into a receptacle and shaken down thoroughly, the particles evidently move—not with perfect freedom

as in a viscous fluid—but rather as a plastic substance, bridging across the space so that the packing is by no means the closest possible. In an actual experiment, after continued shaking for about a half hour, the pore space, as determined by means of carbon tetrachloride, was not 47.64 per cent as with equal spheres and close cubical packing but 81.6 per cent by volume. In an aqueous suspension made with water containing one-tenth of 1 per cent of potassium carbonate the plastic flow was found to begin in a mixture containing 80.5 per cent water by volume.

IV. DISCUSSION OF EXPERIMENTAL DATA

1. LAW OF PRESSURES

We take the data for capillary No. 1, Table 2, Fig. 8, to prove that for a certain medium range of pressures the volume of flow is quite accurately represented by the formula

$$v = K (P - f) \dots \dots \dots \quad (13)$$

where v is the volume of flow per second, f is what we shall denominate the friction constant¹⁰ expressed in grams per square centimeter required to start the flow and determined graphically as the intercept of the volume-pressure curve on the pressure axis as shown in Fig. 8, and K is an arbitrary constant. To test the formula the values of K are given in Table 14.

TABLE 14

No.	P-f	$v \times 10^3$	$K \times 10^6$	Deviation from mean
20	48.8	5.53	116.0	- 0.9
19	50.6	6.14	120.3	+ 3.4
2	76.6	9.06	118.2	+ 1.3
1	78.5	8.95	114.0	- 2.9
7	100.1	11.82	118.1	+ 1.2
3	113.0	9.17	81.1	-----
8	128.1	14.37	112.0	- 4.9
9	128.8	15.49	120.3	+ 3.4
11	156.7	19.97	127.4	+ 10.5
10	157.2	17.66	112.3	- 4.6
4	210.0	23.23	110.6	- 6.3
Av...	116.9	3.9

¹⁰ The term "internal friction" is used sometimes as synonymous with viscosity. There is not only no need for this term but there is positive objection to its use in this connection, since the laws of viscous flow are quite different from the laws of ordinary friction. Since in suspensions we have the collisions of particles with the dissipation of the energy of translation according to the laws of friction, we have here a true internal friction, and it seems best to reserve the use of the term for this case.

Leaving out experiment No. 3, which appears to be grossly in error, we obtain an average value for K of 116.9, with an average deviation from this mean value of 3.9. There is no perceptible drift in the mean value when the experiments are arranged as here

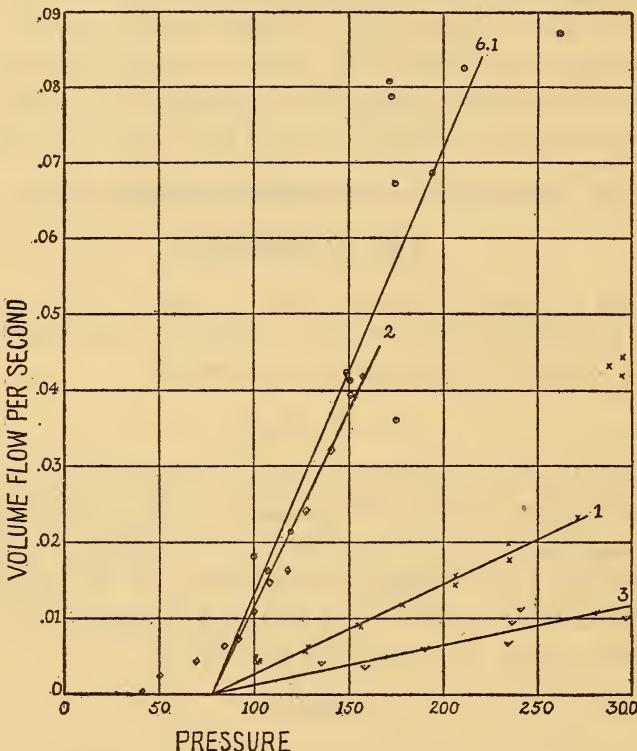


FIG. 8.—The results of experiments at $25^{\circ} C$ with Capillaries No. 1, No. 2, No. 3, and No. 6.1 with 50 per cent by weight of clay suspended in pure water are here plotted. For medium pressures the curves are linear and intersect each other at a point on the pressure axis which is widely removed from the origin. Comparing this with Fig. 2, we see that this affords a sharp distinction between viscous and plastic flow. Capillary No. 1 shows that at high pressure the flow suddenly increases, which is believed to be due to slipping. Capillary No. 2, shows that there may be an increased flow at low pressures, which is probably due to seepages

in their order of increasing pressures or in their chronological order.

If the above law held at all pressures, no flow would occur at pressures less than that equal to the friction constant. Experiments with capillary No. 2 in particular demonstrate that flow does, however, take place below this pressure.

We believe that this flow is of a different character from the flow at the pressures just considered, and that it is associated with a change in concentration due to seepage. Certain it is that even were there no flow en masse, there must of necessity be more or less seepage through and around the material. Such seepage would be a maximum in mixtures with low concentration of solid, since this would increase the size of the pores, and with pressures which are nearly sufficient to cause the flow of the mass as a whole. As this seepage takes place we have noticed, under unusual circumstances, almost pure water flowing out, but very slowly. More usually the seepage causes a change of concentration of the part entering the capillary; this in turn causes a lowering of the friction constant, and consequently the material flows en masse with a minimum of separation but with considerable velocity.

But the question arises, Will there not be seepage even when the pressure is more than sufficient to overcome the friction? Table 15 gives an affirmative answer to this question, but it also indicates that the conditions of flow are unstable, since the values of K vary widely even when the pressure is practically constant. The percentage of clay in the mixture, which had flowed through the instrument and was found by analysis, is given in the last column of the table and serves as an indication of the amount of change in concentration of the original 50 per cent mixture due to seepage.

TABLE 15

No.	$P-f$	$v \times 10^3$	$K \times 10^6$	Per cent clay by analysis
13	2.1	2.45	1165	49.2
18	23.4	4.48	191.3	48.7
14	23.8	5.00	210.0
15	24.3	4.90	201.9
16	24.9	4.21	169.0
17	25.3	4.50	177.8

At high pressures there is also an increase in the rate of flow, but unlike the increase at low pressures it takes place suddenly. Comparing table 16 with table 14, we see that increasing the value of $P-f$ from 192.9 to 210 causes an increase in the value of $K \times 10^6$ from 120 to 209, and the values at still higher pressures are in the region of this higher value.

TABLE 16

No.	P-f	v $\times 10^3$	K $\times 10^6$
5	210.0	43.84	208.8
12	216.3	41.94	193.9
6	217.3	44.87	206.5

From the first it has been apparent that this phenomenon can not be ascribed to experimental errors. It appears repeatedly in the course of this investigation and the phenomenon was some-

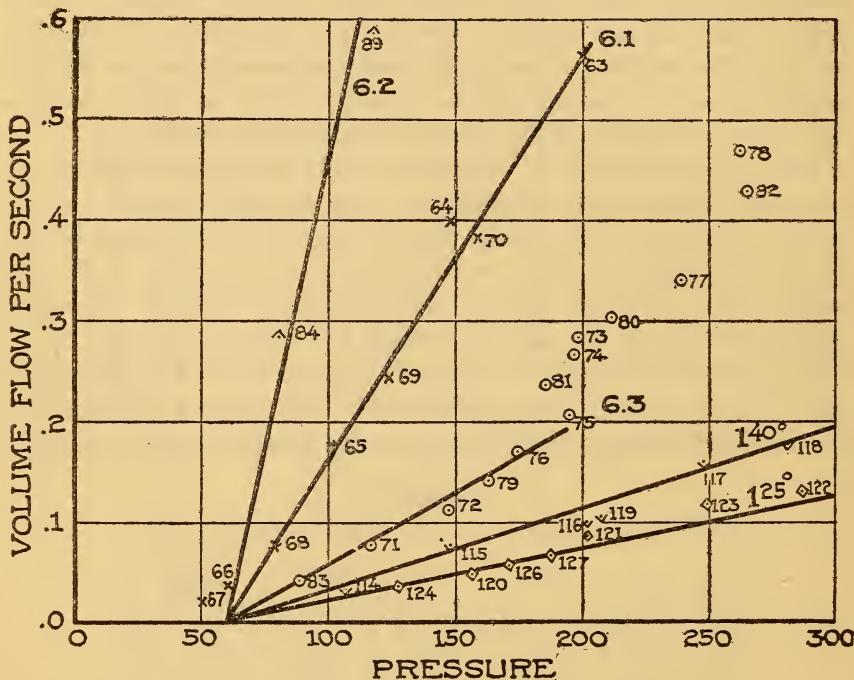


FIG. 9.—The results of experiments at 25° C with Capillaries No. 1, No. 6.1, No. 6.2, and No. 6.3 with 50 per cent by weight of clay suspended in a 0.1 per cent solution of potassium carbonate, and with Capillary No. 1 at 40° C, are here plotted. The friction constant is less and the mobility far greater than in the neutral suspension. Rise in temperature increases the mobility. With Capillary No. 6.3 the results are irregular at high pressures.

what thoroughly investigated when using capillary No. 6.3 and an alkaline suspension. (See Table 7, Fig. 9.)

It occurs to one at once that in fluids there is a change from viscous flow to hydraulic flow as the velocity increases and reaches a certain critical value. However, it is extremely improbable that this change in régime is due to the eddies which cause hydraulic flow, because the total kinetic energy of the material flowing

through the capillaries in our experiments formed a negligible part of the total energy expended. This is shown in column 7 of Tables 2 to 14. The probable cause will be discussed later.

From our analysis of the data for capillary No. 1 given in Table 2, we conclude that the law of pressures expressed by equation (13) holds true for medium pressures, but not for high pressures nor for pressures only slightly greater than the friction constant. This conclusion is confirmed by later experiments, as may be judged from the value of μ in the Tables 2 to 14.

2. FRICTION CONSTANT

The friction is constant to within the limits of experimental error for suspensions in neutral solution, as shown by capillaries No. 1, Table 2; No. 2, Table 3; No. 3, Table 4; and No. 6.1, Table 5. Capillaries 1, 2, and 3 differ from each other very little in diameter but considerably in length, No. 3 being 3.6 times the length of No. 2. Yet the friction is 78 for both. This proves that the friction is independent of the length of the capillary. On the other hand, the radius of capillary No. 6.1 is over twice that of the others. Since its friction is the same, it follows that the friction is independent of the radius of the capillary.

We should expect that decreasing the pressure between the solid particles would also decrease the friction. Hydroxyl ions are well known for their deflocculating power and accordingly the friction in the alkaline solutions is less than in those which are neutral, the friction dropping from 78 to 59.5 in the very weakly alkaline solution used. The experiments with capillaries No. 1, Table 13; No. 6.1, Table 6; and No. 6.3, Table 7, give a value for the friction which is 59.5 to within the experimental error, for 50 per cent suspensions at 25°. Experiments made with the same suspension at 40° using capillary No. 1, Table 12, give the same

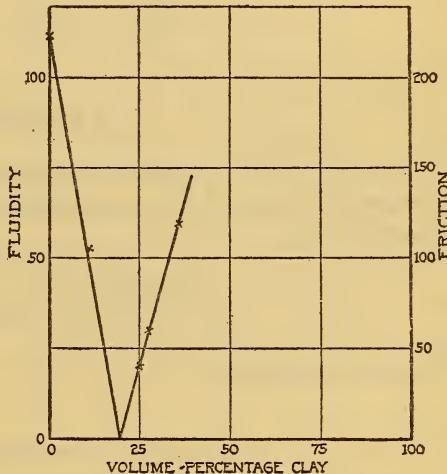


FIG. 10.—As the volume percentage of clay is increased the fluidity rapidly decreases and becomes zero in the 19.6 per cent mixture. At this concentration the friction begins to have a positive value and increases rapidly and in a linear manner, equation (14).

friction. This indicates that the friction is independent of the viscosity of the medium.

The value of the friction varies rapidly as the concentration of the suspension is altered, Fig. 10, but in a linear manner as expressed in the following formula:

$$f' = (b - 0.196) \cdot 718 \quad \dots \quad (14)$$

The values of f and f' are given in Table 17.

TABLE 17

Fraction solid by volume = b	Friction constant observed = f	Friction constant calculated = f'
0.2528	40.0	40.8
.2762	59.5	57.6
.3640	119.0	120.6

3. MOBILITY

Given the law of pressures, we may make the assumptions made in regard to viscous flow and derive the formula, quite similar to equation (1a)

$$\frac{I}{\mu} = \frac{\pi gr^4 t(P - f)}{8V(l + \lambda)} - \frac{m\rho V}{8\pi t(l + \lambda)} \quad \dots \quad (15)$$

For a given capillary

$$\frac{I}{\mu} = C t(P - f) - C' \rho / t \quad \dots \quad (16)$$

where C and C' are constants.

In Tables 2 to 10 the values of the last two terms in equation (16) are given in columns 6 and 7, and the values of μ , to which we refer as the mobility,¹¹ are given in the last column of the tables.

In Table 18 we summarize the data in reference to the mobility.

¹¹ The term "mobility" has occasionally been used as synonymous with fluidity, but for this use it is unnecessary. For the purpose for which it is here employed it is closely related to fluidity but not identical with it.

TABLE 18

Table	Cap. No.	Suspension ^a	Temp., °C	K×10 ⁶	Length	μ	μl
3	2	50 neutral	25	508	1.2195	2.48	3.02
2	1	50 neutral	25	117	2.4680	1.17	2.89
4	3	50 neutral	25	56.3	4.4120	1.02	4.50
5	6.1	50 neutral	25	602	5.0110	0.73	3.66
13	1	50 alkaline	25	521	2.4680	5.11	12.61
8	6.2	50 alkaline	25	2.5094	<7.4	<18.5
6	6.1	50 alkaline	25	4012	5.0110	4.60	23.05
7	6.3	50 alkaline	25	1462	9.9983	3.37	33.7
11	1	47 alkaline	25	2.4680	7.35	18.1
13	1	50 alkaline	25	521	2.4680	5.11	12.61
9	6.2	60 alkaline	25	2.5094	0.119	2.99
10	6.2	70 alkaline	25	0	2.5094	0	0
13	1	50 alkaline	25	521	2.4680	5.11	12.61
12	1	50 alkaline	40	766	2.4680	7.88	19.4

^a The suspensions are expressed in terms of percentages by weight of clay.

From the above table it is clear that the mobility is not constant for the different capillaries, even though the material is identical, but it decreases as the capillary is lengthened. In fact, for the suspensions in pure water, the product of the mobility and the length, given in the last column, yields a much more nearly constant quantity. This taken by itself would indicate that the law of lengths, which holds for viscous flow, does not hold for plastic flow. The data seem to indicate that the volume of flow varies inversely as the *square* of the length of the capillary. However, on closer examination of the data, we find that this can not be the true explanation.

In the first place, the value of the mobility for the alkaline solutions is more nearly constant than is the product of the mobility and the length of capillary, which proves that the volume of flow apparently varies inversely neither as the first nor second nor any fixed power of the length.

In the second place, we recall that at high pressures capillary No. 1 in 50 per cent neutral suspension gave a much higher rate of flow, corresponding to a mobility of about 1.98, which is nearly twice the value taken for the average, or 1.17. Similarly capillary No. 6.1 gave one value as high as 1.63, and on the other hand, capillary No. 2 gave one value as low as 1.92. Now these divergences in our values are far outside of any known error in measurement and we can explain them only by assuming a change of régime in the case of the higher values. We will discuss the nature of this new régime later.

We therefore return to the provisional acceptance of the laws of lengths and diameters for plastic flow which hold for viscous flow and leave for future work the elimination or estimation of the extraneous influence on the flow which is here apparent. (See "Slipping," p. 340.)

Since the mobilities which we have obtained for the suspensions of different concentrations are for capillaries of practically the same length, we may regard the results as truly comparable, although the absolute values may be subject to correction.

In Fig. 11 we have plotted mobility against volume concentration. The curve begins with a very large value at the 19.6 per cent suspension by volume, decreases rapidly and reaches a very small value at about 40 per cent of solid.

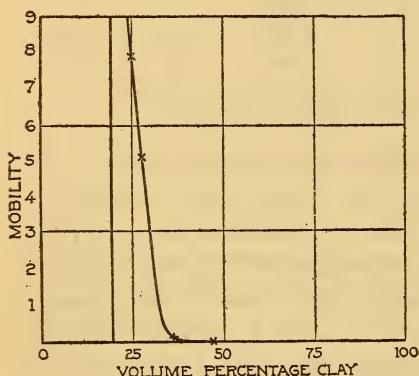
The curvature is very great near this latter concentration, and it is therefore critical as regards the character of the flow. We noted a marked change of appearance as this concentration was passed. In all of the lower concentrations the surface tension was strong enough to cause the material flowing from the capillary to take the form of drops, but in the higher, 47 per cent, suspension, the material for the

FIG. 11.—The mobility decreases very rapidly from the 19.6 per cent mixture, where the fluidity is zero, and the mobility a maximum to a 50 per cent mixture where the mobility is negligible on the scale used

first time flowed out in the form of a wire.

The region of notable mobility is therefore very restricted, even in a very plastic clay. In a so-called "nonplastic" substance, this curve would doubtless be very much steeper. It is also evident that at still higher concentrations of solid than those used here, the flow must be very slight for moderate pressures or else slippage must play an important part. We know that in technical practice, slipping of the type discussed earlier under case 3 is definitely promoted by wetting the die through which the material is forced with some substance having considerable fluidity.

The effect of a 0.1 per cent alkali upon the mobility is even more marked than upon the friction constant, the mobility being raised from 1.17 to 5.11, both suspensions being measured in



capillary No. 1. There is then an increase of over 330 per cent, which is a truly extraordinary effect.

The temperature has an effect upon the mobility which is only less marked than that just considered, but the increase in the mobility as the temperature is raised is readily accounted for by the increase in the fluidity of the medium. The ratio of the mobilities is

$$\frac{\mu_{40^\circ}}{\mu_{25^\circ}} = \frac{7.88}{5.11} = 1.54$$

while the ratio of the fluidities of water at these temperatures is

$$\frac{\varphi_{40^\circ}}{\varphi_{25^\circ}} = \frac{166.9}{111.7} = 1.49$$

The difference between these is a little over 3 per cent, which is easily accounted for on the basis of experimental error.

It seems appropriate to conclude this section with some remarks of a general nature upon mobility and its relation to plasticity.

Any substance which requires a shearing stress of finite magnitude to produce a permanent deformation without rupture is plastic. If infinitesimal stress is sufficient to produce permanent deformation, the substance is viscous. All liquids and gases are viscous, and all plastic substances must be regarded as solids.¹² It does not follow that all solids are plastic, for if on subjecting a body to shearing stress all of the deformation is temporary, the body is perfectly elastic and nonplastic for the stress under consideration. If, on increasing the stress, rupture takes place before there is any permanent deformation, the substance is brittle and totally nonplastic. If the space between two parallel planes at unit distance apart is filled with a plastic substance, and a unit tangential force per unit area be applied in addition to the force required to just overcome the friction, the velocity given to either plane in respect to the other is a measure of the mobility.

We have hitherto avoided the term "plasticity." The conception underlying the word is not only of capacity of a substance for being molded into a desired form, but necessarily of retaining that form when it is once attained. Plasticity is therefore not a simple property. We have seen that the ability of a substance for taking a desired form is dependent upon the mobility and perhaps the slipping, and also upon the friction constant. It is a maximum

¹² Throughout this paper we use the term "fluid" as synonymous with "viscous substance," and the term "solid" as synonymous with the term "plastic substance." We hope later to study the flow of emulsions, foams, metals, etc. At present we are not prepared to discuss these types of flow.

when the friction is zero and the mobility a maximum. On the other hand, the ability of a substance to hold its form is dependent primarily upon the friction constant, but the rate of change of form is dependent upon the mobility. It is a maximum when the friction constant is a maximum and when therefore the mobility is very small.

It is sometimes desirable to strike a balance between the two factors of ease of working and stability of form which is suited to the given conditions. In paint the mobility must be high and the friction may be low, but in pottery material it is necessary that the friction constant be relatively high. As the friction is increased the concentration is finally reached where the pore space is no longer filled with liquid. The material then loses cohesiveness and crumbles.

In the comparison of plastic materials it would appear that the ratio of mobility to friction would have practical importance, but perhaps more important still is the slope of the mobility and friction concentration curves or the range of concentrations between the one in which the friction is zero and the one in which the mobility is negligible.

4. SLIPPING

If the shearing stress exceeds a certain value rupture takes place, quite independent of whether the material is a viscous fluid like pitch or a plastic solid like steel or soft lard. In a heterogeneous mixture like clay suspensions the conditions at the boundary, or slight local changes in concentration, may be the cause of further separation of the solid from the liquid medium, giving rise to the slipping already discussed under case 3, the water forming the lubricating layer. Slipping has never been positively identified in the flow of liquids even after the most painstaking search, but there is no inherent reason why the phenomenon should not appear in plastic flow where the force required is so much greater. We should expect to detect it when the pressure becomes very great or, what is practically the same thing, when the capillary is very short, making the pressure gradient large. It is precisely under these conditions that our experiments give unexpectedly large values for the flow.

In our experiments the unexpectedly large values appeared very suddenly with increasing pressure. Whether or not there are really two curves with a metastable region where they join is not clear at present, but it seems likely that the high values do not fall on a smooth curve.

V. RELATION OF RESULTS TO EARLIER WORK ON PLASTICITY

There are doubtless many types of plastic substances, but for practical reasons the plasticity of clay has received the most attention. Doubtless, however, the observations made in regard to clay have a general application.

In explaining why some clays are plastic and others are not fineness of grain must play the most important rôle, if the views presented in this paper are correct. Fineness of grain alone brings about certain effects which are important.

1. Fine grains result in fine pores when the particles are close together, but water diffuses very slowly through such a material. In a pile of wet sand the water diffuses rapidly and thus the lower portions become weak because of too much water while the upper portions may be crumbling from having too little.

2. Fine-grained material has a far greater pore space than coarse-grained material in the concentration which has zero fluidity and zero friction. There is therefore a greater range of concentrations over which the material is plastic.

3. For a given value of the friction the fine-grained material will contain more of the liquid medium than will a suspension of coarser particles. This greater percentage of water will naturally increase the mobility and the slipping. But since for a given friction the pore space, and therefore the water required to produce plasticity, is greater, we should expect shrinkage on drying. Since, moreover, the diffusion of the water outward will be very slow in the finest material, we should expect that unless the drying is accomplished very slowly the shrinkage would be accompanied by cracking.

4. On drying, the fine-grained material will offer more numerous points of contact between the particles over a given cross section. This will result in a stronger cohesion. The finer the material the more rapidly will salts dissolve out of it. This possible increased concentration of salts, and the fact that there is an increased volume of solution due to the large pore space, makes the amount of cementing substance larger in the fine-grained material.

5. Owing to the slow diffusion through the fine material the medium will tend to become highly concentrated with soluble substances. Furthermore, liquids passing through the fine material will tend to leave behind their larger particles or molecules.

Possibly in this way we may explain the high adsorption and hygroscopicity of plastic clays.

All of the above consequences of fineness of material are found in plastic clays which have been investigated. There are, however, numerous exceptions when we attempt to get anything like a quantitative relation. Since there are several other important variables besides the size of grain, exceptions are to be expected. The theory would lead us to expect that the shape of the grain would have an important bearing upon the plasticity. Furthermore, the size of grain is not easily determinable because the grains are usually of varied sizes. We have already seen that the mobility is affected in a marked degree by the alkaline or acid character of the medium and it may also be dependent upon the specific cohesion between the particles. Moreover, the mobility is dependent upon the fluidity of the medium. This, in turn, is affected by temperature and by substances in solution, either crystalloid or colloid.

For our present purpose it will be sufficient if we show that fineness is the prime factor in producing plasticity. It has been more than suspected for a long time that fineness is a cause of plasticity, but the reason for such a connection has not before been pointed out.

First of all clay, so well known for its plasticity, is not a definite substance. In the mechanical analysis of soils the very *fine* material is called clay regardless of its chemical composition. Merrill¹³ says, in criticism of the current definition of clay—

Kaolinite is itself not properly a clay nor is it plastic. Further, in many cases it is present only in unessential quantities. More open to criticism yet, because more concise, is the statement sometimes made that clay is a hydrated silicate of alumina, having the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$. It is doubtful if a clay was ever found which could be reduced to such a formula excepting by a liberal use of the imagination. There is scarcely one of the silicate minerals that will not when sufficiently finely comminuted yield a substance possessing those peculiar physical properties of unctuous feel, plasticity, color, and odor which are the only constant characteristics of the multitudinous and heterogenous compounds known as clays. Daubree, as long ago as 1878 (*Geologie Experimentale* 1879, p. 25), pointed out the fact that by the mechanical trituration of feldspars in a revolving cylinder with water, an impalpable mud was obtained which remained many days in suspension, and on drying formed masses so hard as to be broken only with a hammer, resembling the argillites of the Coal Measures.

Grout¹⁴ states that "All finely ground substances show this property of plasticity to a greater or less extent." The experiments of Rosenow¹⁵ on the hygroscopicity, heat of wetting, and

¹³ Nonmetallic Minerals, Wiley and Sons, p. 221; 1904.

¹⁴ W. Va. Geol. Surv., 3, p. 38; 1906.

¹⁵ Ton-industrie Zeitung, 35, p. 1261; 1911.

size of grain point to an enormously increased surface in plastic clays. Wheeler¹⁶ has found that nonplastic slates, Iceland spar, propyllite, gypsum, and hallosite can all be made to show apparent plasticity. Stull¹⁷ found that mica ground for 15 hours with water and then screened to 120 mesh "developed a surprising degree of plasticity; in fact, it showed a greater degree of plasticity than some clays which are being worked successfully at the present time. This tends to prove that plasticity in kaolinite is due to fineness of grain and thin plate-like structure." (Cf. also Vogt¹⁸.)

H. B. Fox¹⁹ in the ceramic laboratories of the University of Illinois, separated the grains of a shale and a glacial clay into the several grades of fineness and found that all the grades possessed a plasticity that varied directly with the fineness of the grain, and that the coarse grains which could not be disintegrated by 20 hours of constant shaking in water, when broken down in a mortar, developed plasticity that increased as the size of the grains decreased, until when the coarse grains had been reduced to an impalpable powder they developed a plasticity nearly equal to that exhibited in the finest grains that had been separated from the original sample, showing, it is believed, that the coarser grains were comprised of minerals similar in every respect to those in the fine grains, but cemented in such a way that they withstood successfully the disintegration treatment.

According to Ladd,²⁰ clays can be divided into three classes, as follows:

(1) Those which occur in their place of origin—that is, indigenous clays, which consist of plates, variously aggregated, and prismatic crystals; (2) those which have been transported, broken into cleavage scales, and deposited in degrees of fineness, according to the sorting power of water, moving with different rates of flow; and (3) those which have been indurated either by cementation, recrystallization, or some unknown cause, to the point where they will no longer slack in water. In order to make the clays of the last class plastic, they must needs be first ground. The other two clays are both plastic, the former the least so; while of the latter those which are the finest in grain having been carried the farthest or deposited in the quietest water, are the most plastic of all. These clays differ, respectively, in a marked degree of plasticity according to the amount of interstitial water which they contain. A certain percentage of the latter, differing in the different clays, gives a maximum plasticity.

Johnson and Blake²¹ say, "Plasticity is a physical characteristic and appears to have a close connection with the fineness of

¹⁶ Missouri Geol. Survey, 4, p. 97; 1896.

¹⁹ Purdy, Ill. State Geol. Surv. Bull., 9, p. 182; 1908.

¹⁷ Trans. Amer. Ceram. Soc., 4, p. 255; 1902.

²⁰ Georgia Geol. Surv. Bull., 6a, p. 29; 1898.

¹⁸ Ton-industrie Zeitung, p. 140; 1893.

²¹ Amer. Jour. of Science, 2 ser., 93, p. 351; 1867.

the particles." Bleininger²² remarks that in certain clays "a close and dense structure prevails which does not absorb water until the latter is forced into the pores by grinding and pugging. Clays of this type therefore show but a feeble initial plasticity. * * * It seems to be a fact that plasticity as measured by the ability of the clay to be molded and to flow through dies is dependent upon the development of this water-saturated micellian structure."

Even when the particles of clay are not cemented together there is no reason for their becoming separated from each other spontaneously merely by the presence of water, which at best can only diffuse very slowly through the pores that exist. Yet in order to develop the mobility of the material the close packing must be destroyed and the pores opened up. To effect this, mechanical force must be employed. Thus, there comes about the importance to the ceramist of kneading in the pugging mill, or wetting and drying, and particularly of freezing and thawing.

Grout²³ found that all of the clays tested by him were improved in plasticity by alternate wetting and drying. "Shales ground to 40 mesh weathered to approximately the same figures as the duplicates at 100 mesh. This suggested that the action might be largely mechanical. The amounts of clay (below 0.005 mm) in shale No. 63 were determined before and after weathering. The per cent rose from 7.7 to 17.8 by one wetting and drying."

Rolfe²⁴ states: "When beds of kaolin or of flint clay * * * are exposed to the action of the weather for a sufficient length of time disintegration takes place and the nonplastic material becomes plastic." (P. 28.) Speaking of the minerals in kaolin, he says: "Admixtures of these minerals when pure form a white mass, pulverulent or easily made so by weathering, and but little plastic until finely ground, but its lack of plasticity is probably due to cementation of its grains." (P. 27.) He says of flint clays: "There is a class of clays of almost stony hardness having a conchoidal fracture and a structure so like flint that they are commonly known as flint clays * * *. There is then no necessary relation between the flinty structure and their chemical composition or any physical property except plasticity. All flint clays are nonplastic. Some are rendered more or less plastic by the ordinary grinding and kneading to which clays are subjected, but

²² Bureau of Standards Technologic Paper No. 1, p. 3.

²³ Loc. cit.

²⁴ Illinois State Geol. Surv. Bull., 9, p. 28; 1908.

some are not." (P. 31.) Speaking of gumbo clays, he says: "These are composed of exceedingly fine clay-like material which packs so closely that water passes through it but slowly. It was laid down in still water, the streams which brought it having deposited all sediment coarser than the finest sand and clay, because of loss of velocity, before reaching this point. It is very plastic and possesses great binding power, but dries slowly and cracks badly." (P. 34.)

Beyer and Williams²⁵ state: "Although pure clays, which consist alone of kaolinitic grains are commonly nonplastic, they frequently possess plasticity or may be made to exhibit this property by pulverization and weathering and without any alteration of their composition."

Finally, it may be noted that in adding sand or other nonplastic material to plastic clay the plasticity is lowered less in proportion as the material added is finely divided.

There is at present no reliable means for measuring plasticity. It has been proposed to measure various other properties instead which are supposed to be related to plasticity, such as the amount of water required to bring the clay to a proper consistency, the tensile strength of the wet clay or of the clay after drying, of the adsorptive power of the clay for certain dyes such as malachite green, of the shrinkage on drying, or of a combination of such tests. That there is a relation between plasticity and these other properties is thus generally recognized. Thus Purdy²⁶ states: "Experimental evidence indicates that variation in the fineness of grain controls many of the physical and pyrochemical properties exhibited by clays. Plasticity, shrinkage in drying and burning, tensile strength, drying properties, rate of oxidation, rate of vitrification, toughness of burned ware, and, finally, to some extent, pyrometric value of the clay, are all influenced by fineness of grain."

The following table is compiled from the work of Purdy. In column 1 are given the names of the clays; column 2 shows the relation between the amount of surface in a unit volume for the different clays; column 3 gives the percentage by weight of dry clay particles of diameters ranging between zero and 0.001 mm; column 4 gives the average volume shrinkage in percentage; column 5 gives the amount of water needed to produce maximum plasticity, while column 6 gives the excess of water over and above that required to fill the pores of the dried brick; column 7

²⁵ Iowa Geol. Surv., 14, p. 89; 1904.

²⁶ Illinois State Geol. Surv. Bull., 9, p. 149; 1908.

gives the maximum tensile strength in kilograms per square centimeter. If we multiply the figures in column 8 by 10^{-12} we get an idea of the number of particles in 1 gram of some of the clays used.

TABLE 19

Relation Between Fineness of Grain, Columns 2, 3, and 8, and Shrinkage on Drying, Column 4, Percentage of Water, Column 5, Excess of Water Required to Produce Maximum Plasticity over that Required to Fill the Pores, Column 6, and the Tensile Strength, Column 7

1	2	3	4	5	6	7	8
H 21	783	34.67	18.0	18.0	7.8	9.16	1940
H 23	634	27.30	20.4	21.4	10.3	23.41	1589
K 10	604	25.52	18.3	19.6	8.4	13.24	-----
H 20	553	23.97	16.5	18.3	8.0	8.21	-----
K 4	514	22.24	10.1	16.27	3.6	10.81	-----
I-II	489	21.40	-----	14.4	6.4	13.74	-----
H 18	444	19.22	-----	-----	-----	7.21	-----
K 12	403	15.32	12.7	13.35	5.7	12.97	-----
R 1	397	15.53	13.9	13.4	5.5	11.11	-----
G 21	366	15.72	-----	-----	-----	9.25	-----
K 13	356	13.15	10.5	16.3	3.6	8.35	-----
K 32	341	13.96	10.5	16.82	5.4	9.93	794
K 2	331	13.90	12.2	16.77	4.8	12.29	829
K 11	339	12.94	13.5	-----	-----	9.52	-----
K 7	300	11.81	9.6	17.57	4.9	6.98	-----
R 3	291	11.79	-----	-----	-----	5.22	-----
K 5	287	11.43	5.2	13.06	1.8	5.71	-----
R 4	275	10.85	6.1	13.2	3.9	5.36	-----
K 8	262	10.05	7.5	14.4	3.3	5.36	-----
K 1	256	9.76	6.2	14.9	3.3	7.35	560
K 14	254	9.67	6.1	13.6	2.5	6.71	-----
K 6	221	7.77	10.1	17.03	3.8	8.16	440
K 9	195	7.63	3.5	13.4	1.9	4.37	-----

Since the values in columns 2 and 3 are quite closely parallel, either may be taken as a measure of the fineness of grain. There is certainly a very definite relation between fineness of grain and the amount of water in excess of the pore space in the dried brick required to produce plasticity. There is a relation between fineness of grain and percentage volume of shrinkage, but it is less well marked, and the relation to the tensile strength of the dried material is also clear but even less marked.

Measurements of the tensile strength of the dry material are particularly open to objection as a measure of plasticity, since the tensile strength must depend largely upon the amount of soluble cementing material, which in turn depends upon other factors than the fineness. It has been repeatedly observed that materials

are plastic when ground wet which are nonplastic when ground dry. Probably in each case the plasticity is estimated on the basis of the tensile strength. We understand that the United States Office of Public Roads and Rural Engineering formerly tested materials for their binding power uniformly in both the wet and dry condition, and that it was a universal experience that wet grinding gave the greater binding power. It should not be overlooked that here chemical composition of the material is of importance.

No work seems to have been done on the flow of plastic substances through long tubes as a measure of plasticity. Some work has been done on the flow of such materials through orifices, which corresponds to the conditions necessary for hydraulic flow. The effort has been made to measure the so-called "viscosity" of plastic materials such as paint by means of paddle-wheel viscometers or instruments of that type. It is quite possible that measurements with this latter type of instrument have the highest significance, but it is manifest that instead of expressing the results in terms of "viscosity" they should be based on the application of the laws of plastic flow.

Among the experiments with orifices, Bleininger and Ross²⁷ have shown that the more plastic substances require the most water to render them plastic, but that all require about the same force of 50 pounds per square inch to start the flow. This seems to be equivalent to saying that in their most workable condition all clays should have about the same friction, but since for a given friction the most plastic clays will contain the most water, they will have the highest mobility and slippage.

Simonis²⁸ made some interesting experiments using 40 g of Zettlitz earth made up with 100 g of water and to which were added successive portions of a dilute solution of sodium hydroxide containing 1.795 g per liter. The pressures seem to have been measured in centimeters of water head and the volume of flow in the number of cubic centimeters which would flow in 600 seconds. He measured the flow of 16 mixtures and pure water, designated by the numbers given on the curves in Fig. 12. The amounts of sodium hydroxide added are given in the second column of Table 20.

²⁷ Trans. Amer. Ceram. Soc., 16, p. 392; 1914.

²⁸ Sprechsaal, 38, pp. 597, 881, 1625; 1905.

TABLE 20

Simonis's Experiments on the Flow of Suspensions of Zetlitz Earth through a 2-mm Orifice

					$f = 0.0$	Obs.			
					$f = 0.0$	Calc.			
14	22	{	372	480	720	972			
			520	566	637	871			
15	26	{		744	720	996			
				566	637	871			
16	30	{	636	696	756	996			
			520	566	637	871			
	H ₂ O		538		618	996			
					637	871			

The curves are nearly linear except when the volume of flow is small. The curvature is again probably due to seepage as in our own experiments. The horizontal distance of the different curves from the curve No. 10 is evidently a measure of the friction constant. The values of the friction constant f' as obtained graphi-

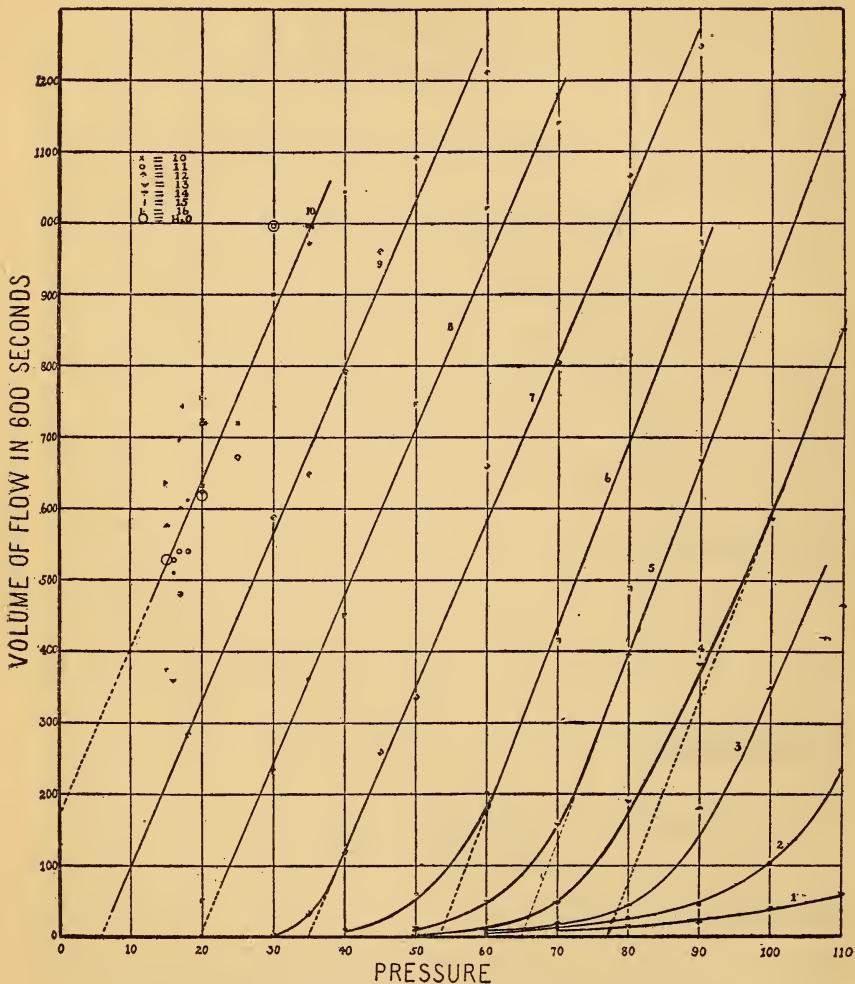


FIG. 12.—Plastic flow from an orifice. Adapted from Simonis

cally are given in the table. We may calculate these values by means of the formula

$$f' = 154 - 14.1 c$$

where c represents the number of cubic centimeters of sodium hydroxide added. It appears, therefore, from a comparison of

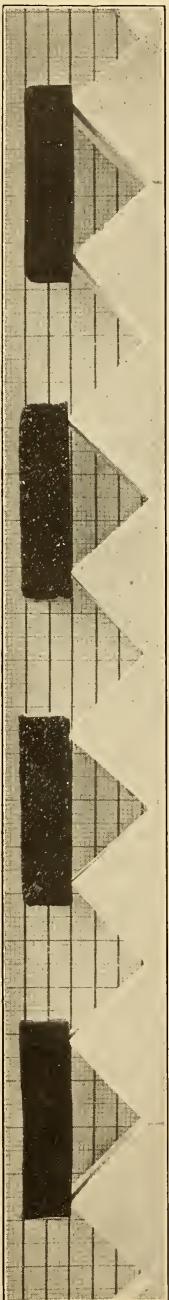


FIG. 13

d

c

b

a



FIG. 14

d

c

b

a

e

the values of f and f' that Simonis's experiments confirm our conclusion from our own experiments that the friction is a linear function of the concentration. We note that the friction constant continually decreases as the water is added until 11 cm³ have been added, after which further additions have no effect upon the rate of flow.

The fact that the curves are sensibly parallel constitutes a remarkable difference between his results and our own. The fact that his curves are parallel signifies that all of the plastic mixtures have the same mobility and that all of the viscous mixtures have the same fluidity, or what amounts to the same thing, the rate of flow is independent of the fluidity or mobility. This is characteristic of the flow through an orifice, where the rate of flow, as calculated from equation 1a or equation 15, is

$$\frac{V}{tk} = \pi r^2 \sqrt{\frac{pg}{m\rho}},$$

since l is equal to zero. It appears, therefore, that Simonis's experiments are to be regarded as a study of the hydraulic flow of plastic materials.

We can calculate the higher rates of flow quite accurately by means of the formula

$$U = 23.4 (P - f') + 168.7$$

as seen in Table 20. The agreement between the observed and calculated values decreases as the rate of flow is lowered.

VI. MODELS OF PLASTIC FLOW

It was thought that the views of the nature of plastic flow here presented might be more convincing if a working model could be constructed. Ottawa sand of specific gravity of 2.638 and 20 to 30 mesh was found to have a pore space of 34.5 per cent. Coal-tar pitch of specific gravity of 1.28 was added to two portions of the sand to the extent of 30 and 40 per cent by volume. These materials after being thoroughly mixed were made into briquettes 4 by 1 by 1 cm and laid on two supports 3.3 cm apart. In Figs. 13 and 14 a briquette of the pure pitch is shown at *a*, the second photograph being taken 28 days later than the first. It is evident that the pitch is a viscous liquid since it flows readily under the very small force here exerted by gravity. The material with 40 per cent pitch, (*b*), is only less fluid, being still viscous, as shown by the

marked sagging. The material with 30 per cent pitch (*c*) is still less fluid, but it can hardly be called plastic since there is very perceptible sagging, and yet the pitch is considerably less than sufficient to fill the pore spaces completely, so that the material is lacking in strength. It may be said therefore that the coarse sand is nonplastic.

Some of the coarse sand was ground and passed through a 20-mesh sieve, and with this briquettes were made containing 40 and 45.5 per cent of pitch. We see in Fig. 14 (*d*) that with even as high as 45.5 per cent of pitch the fluidity is very slight. With 40 per cent (*e*) we have a truly plastic material since now after the elapse of several months the sagging is hardly perceptible. And it may be added that the material has very great strength.

VII. SUMMARY

1. The various types of viscous and plastic flow have been considered theoretically. According to the circumstances of the flow the viscosities may be additive, the fluidities may be additive, or slipping or seepage may enter in to affect the character of the flow. The possible separation of the components of a mixture by means of flow has been considered. It has been shown that in a suspension of solid particles in a liquid there must be a dissipation of energy when the solid particles collide, as they must collide if the layers of the suspension move over each other. This dissipation of energy follows the laws of ordinary friction and not the laws of viscosity.

2. Measurements have been made upon the flow of clay suspensions of different concentrations through capillaries of varying dimensions and at two temperatures.

3. It is shown that plastic flow can be sharply differentiated from viscous flow by the "friction" necessary to start plastic flow. The friction is a linear function of the volume concentration. It is also affected by the presence of alkalies or acids, but it is independent of the length or diameter of the capillary as well as the temperature of the medium.

4. For medium pressure the rate of efflux is given by the formula

$$v = K(P - f),$$

where P is the pressure, f is the friction, and K is an arbitrary constant. The experiments indicate that at low pressures seepage takes place causing a perceptible change in the concentration, and

that at high pressures there is slipping which under certain circumstances may cause a sudden increase in the rate of flow.

5. The fluidity becomes zero at the concentration of solid where the plastic flow begins; that is, where the friction begins to have a positive value. This concentration, where the particles are able to form a bridge across the capillary space, is reached long before the concentration corresponds to close packing of the solid particles. For very fine-grained material the range between the concentration giving zero fluidity and the concentration corresponding to close packing will be much greater than in coarse-grained material.

6. The "mobility" of suspensions has been defined and calculated. The mobility decreases very rapidly from its maximum value in the concentration which has zero fluidity to a value not far from zero in the mixture which corresponds to close packing of the solid particles. The mobility increases with the fluidity of the medium, but it is also greatly affected by the presence of alkalies or acids.

WASHINGTON, March 2, 1916.

