

Some Physical Properties of Wiping Solders *

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The plasticity of a number of solders at wiping temperatures has been determined by compression tests between parallel plates. The character of the flow is found to be that corresponding to a linear relation between shearing stress and a fractional power of the velocity gradient. This corresponds approximately to a relation between rate of compression (dh/dt) and sample height (h) given by the equation: $dh/dt = kh^b$, in which k and b are constants, of which b is independent of the test conditions. For viscous materials $b = 5.0$; for most solders b is greater than 5.0, and increasing values of b are associated with lower temperature gradients of plasticity. It is shown that a solder must have a low temperature gradient of plasticity in order to be properly wiped, and that determination of the value of b by means of a plasticity test can therefore be used to evaluate the working properties of a solder.

A number of factors upon which the plasticity of wiping solders and the porosity of wiped joints may depend have been investigated. In particular, it is shown that segregation is not responsible for porosity, but that the latter may be dependent upon the particle size of the solid phase at wiping temperatures. The relation of particle size to the wetting power of the liquid phase is discussed.

A WIPING solder is one used in joining sections of lead (or lead alloy) piping or sheathing, such as that used for telephone cables. As such, it must wet the sheathing readily, must be coherent and plastic enough to be worked with the hands over a considerable temperature range, and must form a strong, non-porous joint. The desirable qualities for a wiping solder have been more fully enumerated by Schumacher and Basch,¹ but the above will suffice for consideration in connection with this paper.

One phase of a general investigation of wiping solders has been a study of their plastic properties in the temperature range in which they are wiped. In this study consideration has been given not only to the working properties which a solder must have in order to be properly wiped, but also to certain other properties which may affect the character of the wiped joint, particularly those which may result in porosity of the joint.

The temperatures at which the tests described below were made lie in the wiping range, and are intermediate to those represented by the solidus and liquidus lines in the respective equilibrium diagrams of the solders investigated. At such temperatures the alloys form two phase

* Presented before the Society of Rheology, Rochester, New York, December 28, 1931. Published in *Jour. of Rheology*, January, 1931.

¹ E. E. Schumacher and E. J. Basch, *Ind. & Eng. Chem.*, **21**, 16 (1929).

systems, in which a solid phase, composed principally of one constituent, is dispersed in a liquid phase, whose composition and abundance is a function of the temperature and the gross composition of the alloy. These facts suggest that the character of a solder may be related in the wiping range to the following properties: solid-liquid ratio, solid particle size, viscosity of the liquid phase, tendency to segregation, and the interfacial tension between solid and liquid phases.

OBJECTS OF INVESTIGATION

The objects of the investigation may be summarized under the following headings:

1. *Character of Flow:* It was hoped that by means of plasticity determinations, data would be obtained permitting the flow of the various alloys to be formulated in simple terms, and that appropriate flow constants could be evaluated which would suffice to describe the nature and extent of deformation under specified conditions of stress. This object was largely realized through the discovery that the flow is similar in character to that of many colloidal dispersions, corresponding approximately to what would be expected if a power relation exists between stress and velocity gradient.

2. *Relation of Plasticity to Workability:* The primary purpose of the plasticity studies was to determine if the information thus obtained could be related to the working characteristics of the solders. If a clear-cut relation could be found, the plastometer could be employed in testing new alloys for use as solders, and in making control tests on solders as supplied to the splicers. As a matter of fact, a simple relation between the plasticity data and workability was found to exist, on which can be based a method of employing the plastometer in research studies of solders. In addition the plasticity appears to be very sensitive to composition changes, and its measurement with the plastometer should in consequence be useful as a control test. Whether this latter possibility can be realized in engineering practice has not, as yet, been ascertained.

3. *Plasticity and Solid-Liquid Ratio:* Early in the investigation it was suggested that the plasticity might be related to the solid-liquid ratio. If this were so, the plasticity and its temperature gradient could be predicted from the equilibrium diagram for any particular alloy, and calculation of solid-liquid ratios could be used to supplant or to corroborate plasticity determinations. While for any one solder, of course, the plasticity increases with the ratio of liquid to solid, no relation common to any group of solders was found to hold between plasticity and the solid-liquid ratio.

4. *Porosity*: At the start of the investigation it was thought that the porosity of the joint might be related to the plasticity of the solder. As this was not found to be the case, other factors which might be responsible for this condition were investigated. In particular, experiments were performed to determine if porosity is dependent upon segregation, or if it is related to the particle size of the solid phase at wiping temperatures. Porosity and segregation were found to be quite independent, but a relation between porosity and particle size was found in the two tests made in this connection.

Experimental work directed toward these objects has involved the following groups of experiments:

1. Plasticity studies.
2. Segregation studies.
3. Investigation of particle size.

The first of these groups was planned to cover the first three objects enumerated above, while the other two groups are of interest in connection with porosity.

ALLOYS INVESTIGATED

Six different alloys were tested as described in Table I. In this table, the compositions sought in preparing the samples are given, together with the composition found by analysis at the top and bottom of the cast (T & B), except for solders Nos. 5 and 6, of which no analyses were made.

Nos. 2 and 3 are good, workable solders giving non-porous joints, with No. 3 possibly being given preference in ease of handling while the joint is being wiped. No. 1 is also satisfactory from the standpoint of workability, but the joints formed from it are often porous, while the splicers described it as being somewhat "coarse." No. 4 is unsatisfactory in all respects. Some tests on No. 5 showed it to be good, but in recent tests the workability has been poor and a number of porous joints have been found. Solder No. 6 seemed to be fair both in workability and porosity, but the number of tests has been altogether too limited for definite conclusions to be drawn. The workability of neither of these last two solders is as good as that of the lead-tin and lead-tin-cadmium alloys. The results of wiping and porosity tests are summarized to the right of Table I.

A point which the authors wish to stress is that they are interested here only in two of a number of factors which may affect the utility of solders; namely, workability and porosity. Therefore, that a solder is good in those respects does not necessarily imply that it is a good solder in a general sense, and leaves open the question as to

TABLE I

	Per Cent Pb	Per Cent Sn	Per Cent Cd	Per Cent Bi	Per Cent Zn	Workability	Lack of Porosity	Tested at ° C.
Solder No. 1.....						Good	Porous	196, 204 and 210
Desired.....	65	35						
Actual T.....		34.50						
Actual B.....		34.62						
Solder No. 2.....						Good	Good	183, 185 and 194
Desired.....	60	40						
Actual T.....		40.32						
Actual B.....		40.69						
Solder No. 3.....						Excellent	Good	170, 184 and 192
Desired.....	67	24	9					
Actual T.....		24.00	9.28					
Actual B.....		24.13	9.38					
Solder No. 4.....						Poor	Porous	
Desired.....	60			40				
Actual T.....				40.25				
Actual B.....				40.20				
Solder No. 5.....						Fair	Porous	149, 153, 157, 161
Desired.....	67		4.25	28.5	.25			
Solder No. 6.....						Fair	Good	140, 148, 156, 160
Desired.....	65	13		22				

T = Top of cast.

B = Bottom of cast.

whether or not consideration of other factors may show it to be unsatisfactory as a wiping solder.

PLASTICITY STUDIES

Experimental Procedure

The plastometer used in the investigation is a modification of the instrument used by Williams² in studies on rubber compounds. It has been fully described elsewhere³ by one of the writers. A heat-insulated cylindrical steel block provided with heating elements and thermocouples contains a central cylindrical well $2\frac{1}{2}$ inches (6.35 cm.) in diameter and 5 inches (12.70 cm.) deep. The block itself is about 12 inches (30.48 cm.) in diameter, being made large to prevent rapid temperature fluctuations. A flat-bottomed cylindrical plunger, also carrying heating elements and a thermocouple, fits into the well with a small clearance. The load on the plunger may be adjusted to suit the conditions of test. A sample of the material to be tested is placed under the plunger, given 90 minutes to come to temperature and the plunger released and allowed to compress the sample. The

² I. Williams, *Ind. & Eng. Chem.*, **16**, 262 (1924).

³ R. L. Peek, Jr., "Parallel Plate Plastometry" (now being prepared for publication).

temperature is frequently checked, and can be controlled within $\pm 1^\circ$ C. by adjusting external resistances. The sample height is measured at intervals by an Ames gauge which moves with the plunger, a complete record of sample height vs. time being thus obtained. With one exception, the tests here reported were continued for 30 minutes.

The sample size used was one which has been found convenient—a cylinder 1.374 inches (3.490 cm.) in diameter and .300 inch (.762 cm.) high. Samples were obtained from a single cast of each solder, tested for blow-holes and inclusions by density measurements. Samples were milled to dimensions with a tolerance of $\pm .001$ inch (.0025 cm.). The weight of the plunger and load was 30 lbs. (13.63 kg.).

Character of the Flow

The data directly obtained in a typical run, readings of sample height vs. time from start of run, are plotted in Fig. 1, together with tangents to the curve fitting the points plotted. By computing the slope of such tangents there are obtained values of the rate of compression, dh/dt , corresponding to various values of sample height, h . If these are plotted logarithmically, $\log dh/dt$ vs. $\log h$, as in Fig. 2, a straight line is obtained. This shows that under the test conditions employed, the relation between sample height and rate of compression is of the form:

$$\frac{dh}{dt} = kh^b, \quad (1)$$

where k and b are empirical constants. All the tests made on solders gave results that could be fitted with an equation of this type. At any one temperature the value of b was constant for a given solder, while the value of k varied with the load and sample volume but was independent of the initial sample height. A limited number of tests have indicated that all runs made on any one solder at a given temperature can be represented by an equation of the type:

$$\frac{dh}{dt} = K \frac{W^a h^b}{V^c}, \quad (2)$$

where W is the load, V the sample volume and K , a , b , and c are constants characteristic of the material.

It has been shown both theoretically⁴ and experimentally^{3, 5} that

⁴ O. Reynolds, *Phil. Trans., Lond.*, **177A**, 157 (1886).

⁵ Ormandy, "The Engineer," **143**, 362, 393 (1927).

a cylindrical sample of a viscous material is compressed between parallel plates at a rate given by:

$$\frac{dh}{dt} = \frac{2\pi}{3\eta} \frac{Wh^5}{V^2}, \quad (3)$$

where η is the viscosity. This equation is of the form of Equation 2 with $b = 5$. In the solder tests, the values of b obtained were in general much larger than 5.0, so that these materials are not strictly viscous. On the other hand, the fact that the results are independent of the initial sample height indicates that the rate of flow is independent of the strain; while the fact that the curves of $\log dh/dt$ vs. $\log h$ continue to be linear at very low rates of flow indicates the absence of any yield point, or minimum stress required for flow. Hence the stress required for compression appears to be of the type which has been called quasi-viscous—wholly dependent on the velocity gradient.

Flow of this type, of which viscous flow is a special case, has been observed in colloidal solutions tested by the capillary tube method. In such solutions deWaele⁶ found the rate of efflux proportional, not to the pressure (as in strictly viscous fluids⁷), but to a power of the pressure. Porter and Rao⁸ have shown that this would be the case if it were assumed that the shearing stress (τ) is proportional to a power of the velocity gradient (dv/dx), or $\tau = \eta' (dv/dx)^{1/n}$, where η' and n are constants; dv/dx is the velocity gradient normal to the plane in which τ is the tangential stress. Assuming this relation, the case of compression between parallel plates has been shown³ to be given by:

$$\frac{dh}{dt} = C \frac{W^n h^{\frac{5(n+1)}{2}}}{V^{\frac{3n+1}{2}}}, \quad (4)$$

where C is a constant inversely proportional to η' . The development of Equation 4 employs approximations corresponding to those used in obtaining Equation 3, involving the assumption that the diameter of the sample is large compared with its height.

As a matter of at least theoretical interest a series of runs were made on one solder (No. 2) employing different loads and sample volumes, and the data thus obtained were analyzed with reference to their agreement with Equation 4. This analysis is given in an appendix

⁶ A. de Waele, *J. Oil & Color Chem. Assn.*, **6**, 33 (1923).

⁷ Bingham, "Fluidity and Plasticity," McGraw-Hill.

⁸ Porter and Rao, *Trans. Faraday Soc.*, **23**, 311 (1927).

to this paper, and shows that all runs could be fitted without significant variation by an equation of the form of Equation 1, and that the values of b for these different runs did not differ significantly from one another. On the other hand, the values of k thus obtained did differ significantly from an expression of the form $k = K(W^a/V^c)$, in which K , a , and c were selected to give the best agreement with the data, indicating that Equation 2, as applied to this material, is not strictly correct. The values of a and c thus obtained differed considerably from the values of n and $(3n + 1)/2$ respectively that would be required if Equation 4 applied, n being given by equating b to $5(n + 1)/2$ in accordance with this equation. On the other hand, these differences were not indicated as necessarily significant, so that it appears that Equation 4 applies to these data to a fair approximation, the divergence being perhaps due wholly to the approximations employed in the theoretical development.

Regardless of the accuracy of Equation 4, the considerations discussed above indicate quite clearly that the flow of solders in the wiping range is quasi-viscous (independent of strain, and of a yield point requirement) and hence similar to the flow of many colloidal solutions. This conclusion is in agreement with the fact that at these temperatures solder consists of a solid phase dispersed in a liquid phase. It is furthermore apparent that the quantity $b - 5$ (or of $1 - n$, if use is made of the theory given) is a measure of the departure of the material from a strictly viscous condition.

Evaluation of Flow Constants

With the exception noted above, the runs made with the various solders tested were confined to a single sample size and a single load. In each case values of b were obtained by plotting $\log dh/dt$ vs. $\log h$, values of the former quantity being found by plotting tangents as described. To illustrate the reproducibility of points in the plot of log rate vs. log height, Fig. 2 has been prepared from Fig. 1. Curves I and II of Fig. 1 were plotted to different scales of sample height and the tangents drawn. In Fig. 2 are plotted values of $\log dh/dt$ against $\log h$ from the two curves. It is seen that the line would be drawn in practically the same place if either set of points was taken alone.

In comparing solders it is evident that the sample height after a given time is a rough measure of relative consistency, the softer material showing the lower sample height. But from Equation 1 it is evident that such a comparison may be misleading for materials showing different values of b . This is brought out in Fig. 3, in which

are given the height vs. time curves for two different solders. It will be seen that the curves cross each other, and that the consistency of such samples would, if rated on such a basis, depend upon the time selected for the comparison. In comparing two solders tested under the same conditions, consideration must be given to both constants of Equation 1 (k and b). For purposes of qualitative comparison an equivalent procedure is to consider the sample heights at two different times for each sample listed.

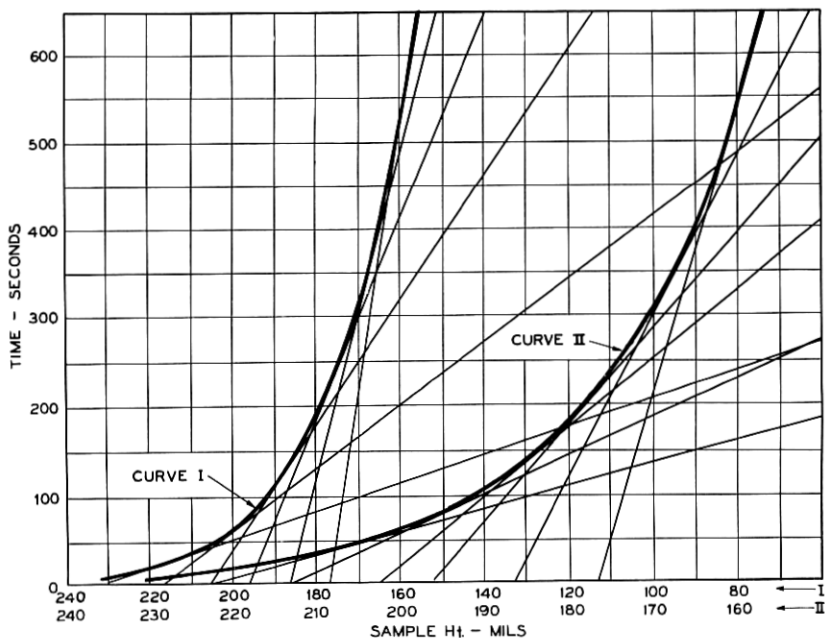


Fig. 1—Plot of a typical set of plasticity data. Solder No. 5—157° C.

Comparison of Plasticity with Solid Liquid Ratio

A summary of the results of the plasticity tests is given in Table II. In this are included values of the percentage of liquid present in the solder at the test temperature, calculated from the equilibrium diagrams by the method advocated by Tammann.⁹

Sample heights after 30 minutes of compression are plotted in Fig. 4 against per cent liquid phase present under the conditions of test. As one would expect, the points for any given solder can be placed on a smooth curve, in which an increase in the proportion of liquid phase

⁹ Gustav Tammann, "A Textbook of Metallography."

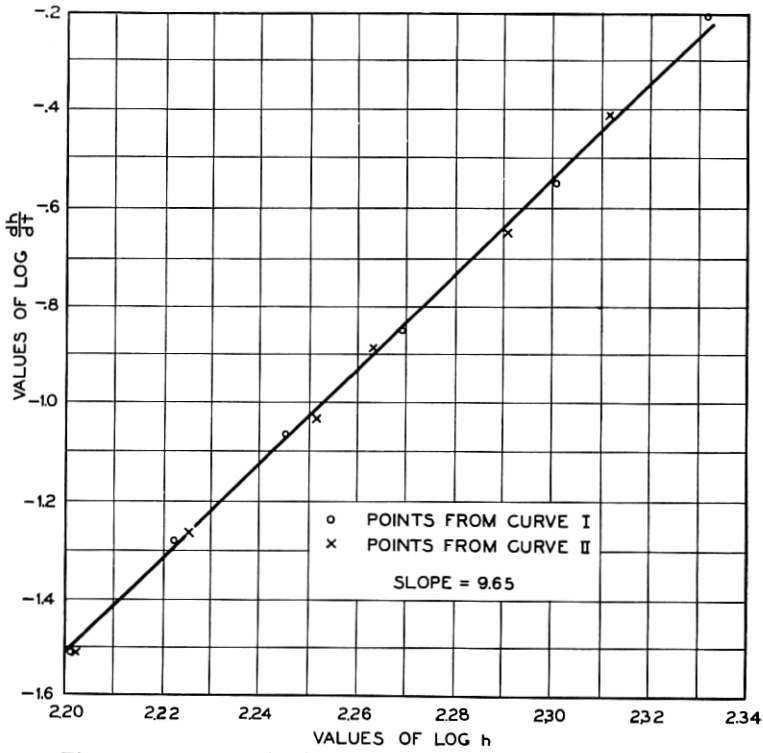


Fig. 2—Log rate vs. log height curve plotted from data of Fig. 1.

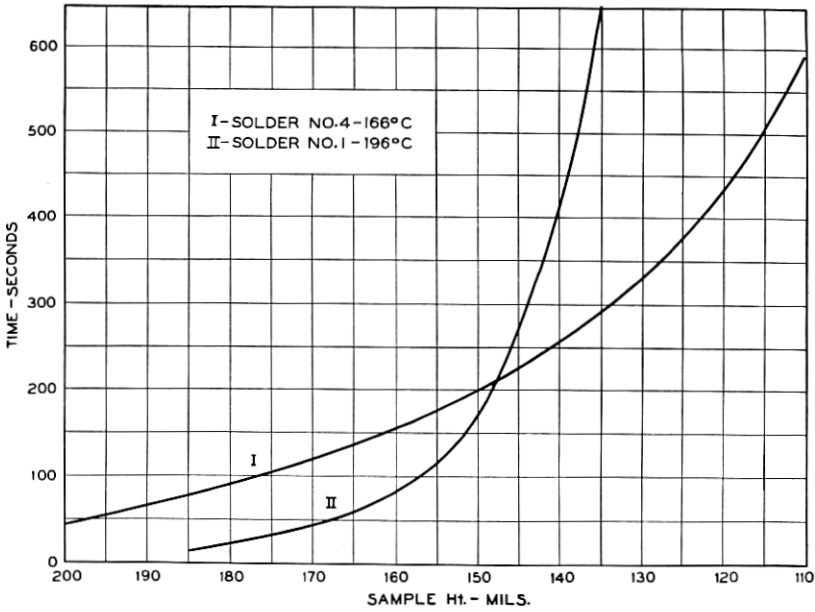


Fig. 3—Effect of type of flow upon sample height vs. time curves.

TABLE II
RESULTS OF PLASTICITY TESTS

Solder	Temperature °C.	Sample Height 1 Min.	Sample Height 10 Min.	Sample Height 30 Min.	Per Cent Liquid *	<i>b</i>	Average <i>b</i>
No. 1.....	196	162	132		47.5	14.58	16.0
	204	145	125	116	51.7	19.12	
	210	117	104	94	55.1	14.20	
No. 2.....	183	150	128	118	52.4	15.80	16.2
	185	143	124	114	53.4	15.56	
	194	127	111	103	57.8	17.24	
No. 3.....	170	132	118	110	43.4	25.60	21.0
	184	130	114	105	51.2	18.14	
	192	115	101	93	55.8	19.30	
No. 4.....	162	266	245	203	55.5	3.88	3.73
	166	197	110	83	59.4	3.58	
	170	42	33	29	62.4	†	
No. 5.....	149		255			6.02	8.24
	153	245	198	166		6.39	
	157	200	158	140		9.65	
	161	185	154	127		10.90	
No. 6.....	140	262	244	224		12.3	13.5
	148	214	175	156		10.2	
	156	164	139	127		15.9	
	160	143	124	115		15.6	

* Equilibrium Diagrams used:

Solder No. 1 and 2—Rosenhain & Tucker.

Solder No. 3—Stoffel.

Solder No. 4—International Critical Tables, Vol. IV.

† Sample heights taken were too low to render the data significant.

corresponds to a decrease in the sample height at any specified time. However, the curves for the different solders do not fall together. As a matter of fact, no such agreement would be expected after studying results such as those plotted in Fig. 3. The curves given in this figure show that if a number of solders are tested at temperatures corresponding to a given solid-liquid ratio, they may fall in quite different orders with respect to each other in a comparison of sample heights, according to the time chosen for the comparison.

Still less agreement among the solders is shown when values of *b* are compared with percentage of liquid phase. There seems to be no relation here; in fact, for a given solder alteration of the temperature and hence of the proportion of liquid phase, does not seem to have much effect upon the value of *b*.

A survey of the curves and data shows that the possibility of drawing

any conclusions from the solid-liquid ratios regarding the plasticity to be expected or regarding the quality of the solder must be dismissed.

Comparison of Workability and Temperature Gradient of Plasticity

In Fig. 5 are shown the plasticity-temperature gradients for the various solders. Here comparative values of plasticity for any one solder are taken as given by the sample heights after ten minutes of compression. It is seen that solders No. 1, 2 and 3 show good (low) gradients, with No. 3 seeming to be superior, while Nos. 5, 6 and especially No. 4, show a large variation in plasticity with temperature. Since, if it is to be properly worked, a wiping solder must not vary rapidly in consistency with temperature, this can be used as one criterion for choosing a satisfactory solder, and on this basis the solders tested should be placed in an order consistent with Fig. 5.

Such a rating is quite in agreement with actual working characteristics, which rank solder No. 3 first, No. 4 last, the others falling in between in essentially the order which Fig. 5 would indicate.

It is now of interest to determine if there exists any relation between the rapidity with which the plasticity varies with temperature and the values of b , the slope of the log rate vs. log height curve. Reference to Table II will show that there is a wide divergence in the values of b found for the different solders. It is further seen that the difference exhibited from one alloy to the next is greater than the difference between individual runs on one solder at different temperatures. This virtual constancy of b for any one solder justifies, it may be noted in passing, the use of sample heights after fixed intervals of compression as comparative measures of plasticity, as in Figs. 4 and 5. There would be no such justification for using such sample heights in comparing different alloys having different values of b .

If then b is regarded as a constant for any one solder, independent of temperature, mean values of b for each solder may be computed from the values obtained at different temperatures. Such mean values have been computed, and are included in Table II. Comparison of these with the curves of Fig. 5 shows a striking agreement between the order of the solders based on increasing temperature gradients and that based on decreasing values of b . This suggests that the temperature gradient of plasticity is the lower, the more removed is the character of the flow from that of a strictly viscous liquid. Furthermore, it is apparent that if the value of b is an inverse measure of the temperature gradient of plasticity, and if the latter is in turn an inverse measure of the workability of a solder, then the value of b is a direct measure of workability.

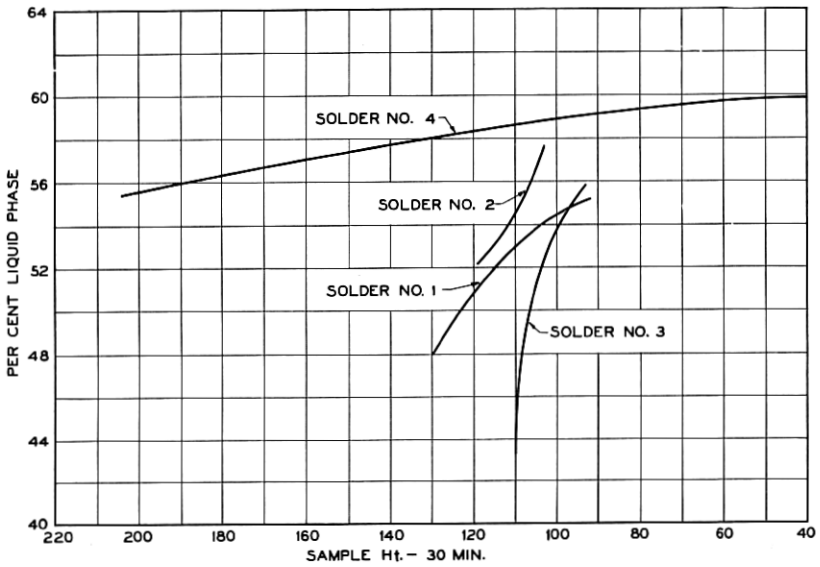


Fig. 4—Relation of plasticity to per cent liquid phase in four of the solders tested.

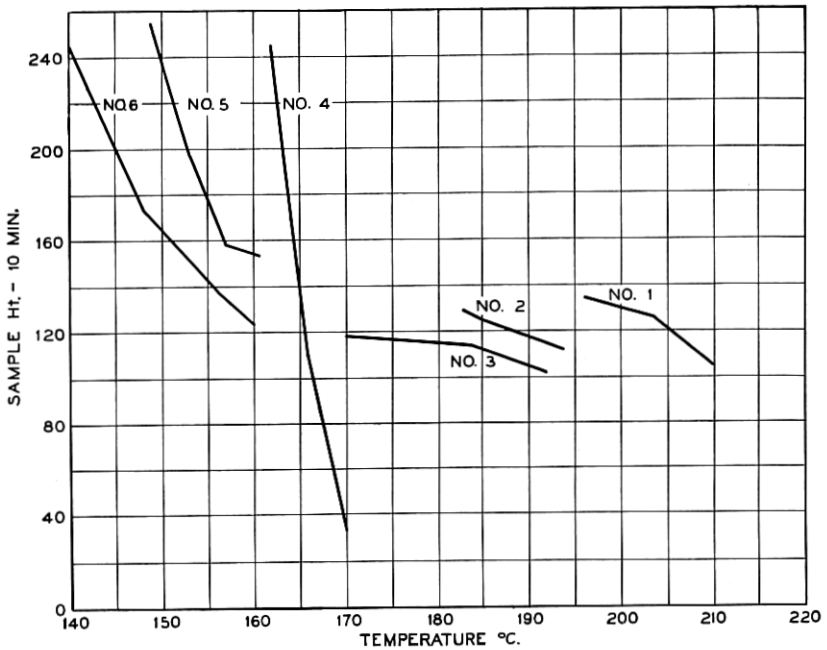


Fig. 5—Variation of plasticity with temperature, showing the superiority of solders Nos. 1, 2 and 3.

As the value of b can be determined in a single test with the plastometer, its relation to workability should permit of the rapid evaluation of the latter property, provided the relation holds in general. Applying this criterion to the solders tested, No. 4, showing virtually a viscous type of flow, ($b = 5$), would be at once thrown out. Solder No. 3 would be classed as a superior solder from the standpoint of workability. Nos. 1 and 2 could be classed as satisfactory. The use of Nos. 5 and 6 would be questionable, with No. 6 having the best chance for success. Practical tests on these last two solders are insufficient to completely confirm this classification, but general indications are that it is correct. Practice has completely confirmed the classification of the other four.

Usefulness of Plastometer in Research and Control Testing

It is believed that the work which has been done on these six solders has furnished information which justifies the use of the plastometer in the future when any group of alloys is to be investigated as to working properties. It appears that the principal demand upon a workable solder is a wide temperature range in which it can be worked. Whether or not a solder is suitable in this respect can very well be determined by the plastometer either by making runs at several temperatures or by determining b at some temperature representative of the wiping range.

A further possible use of the plastometer is in testing solders manufactured or purchased subject to requirements as to their composition. As a rule, the sample height after a given time of compression is quite different for alloys differing in composition. This is illustrated by the curves of Fig. 6, which represent the data obtained with the plastometer on a number of alloys. These show that such a test of composition would not be infallible in a wide application, as the quite dissimilar alloys C and F give quite similar curves. In distinguishing an excess or deficiency of one component in any given series of alloys, however, the test should be quite sensitive.

If the plastometer were used for this purpose, the allowable limits of composition would correspond to limits of sample height in satisfactory samples. Consider, for example, the case of a lead-tin solder of a composition between that of solders Nos. 1 and 2. A convenient temperature of test would be 195° C. At this temperature, the sample height after ten minutes would be 110 mils for a solder of composition 65 per cent Pb, 35 per cent Sn, and 137 mils for one of composition 60 per cent Pb, 40 per cent Sn. Since the plastometer results are reproducible within 2 mils, the accuracy in detecting variation in

composition should be easily within 0.5 per cent. Whether the possible usefulness of the test could be realized economically in engineering practice has not as yet been ascertained.

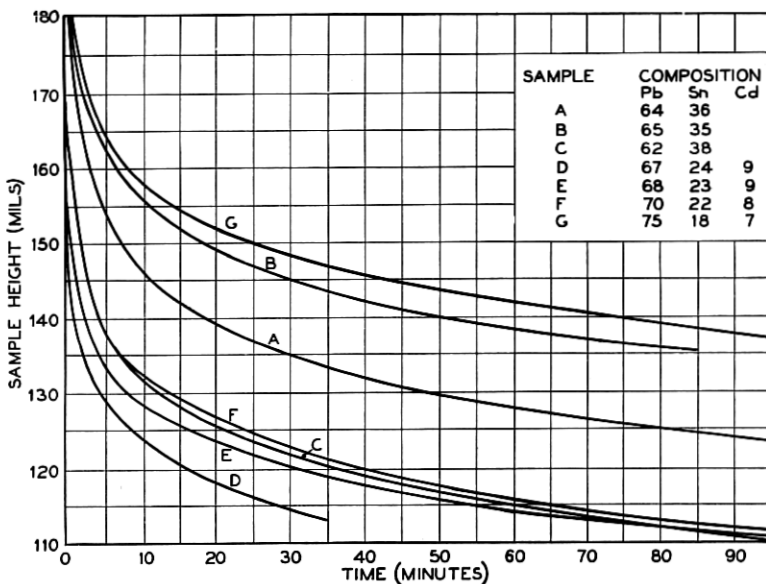


Fig. 6—A group of plasticity curves illustrating the effect of composition upon plasticity.

SEGREGATION

Experimental Determination

The plastic deformation of a material composed of solid and liquid phases, such as a solder during wiping, presents a condition favorable to segregation, and this phenomenon has often been thought to play an important role in determining the quality of a solder. Especially has this been true in regard to porosity. Now, if a sample of solder which has a tendency to segregate is subjected to a plasticity test, a considerable amount of liquid phase should be pushed to the outer edges of the sample during the first part of the run. Since the liquid phase always contains that part of the sample which later solidifies as the eutectic, it follows that after the sample has been allowed to cool, the outer edges should be richer in eutectic than the central portion.

This, as a matter of fact, was found to be true, and measurements of segregation were made upon a number of samples taken from the plastometer. These samples were usually about 5 cm. in diameter. They were cut diametrically, polished and etched.

Photographs were taken with a magnification of 25 ×, which allowed 0.5 cm. of the sample to be photographed at one time. Three photographs were taken along the radius of each sample, one bordered by the axis of the sample, one by the edge, and one mid-way between these two.

These photomicrographs were placed in a beam of light of constant intensity. Since the eutectic appears as a light background, while the particles which separate out as solid above the eutectic temperature appear dark, the light transmitted through the plate is a comparative measure of the relative amount of eutectic present in different parts of the sample. The variation in light transmitted as the picture is passed before the beam therefore indicates the amount of segregation. The transmitted light was directed on a caesium photo-cell and the amplified photo-electric current measured, four measurements being required to span each plate, making twelve measurements on each sample.

Table III gives the results of these measurements. In this table, only the averages of the four measurements of each photomicrograph are given.

TABLE III
SEGREGATION MEASUREMENTS
Light Transmitted Measured in Milliamperes of Amplified Photo-electric Current

Sample		Light Transmitted—Ma.		
Solder	Temp. ° C.	.25 cm. from Center	1.25 cm. from Center	2.25 cm. from Center
1.....	204	0.36	1.08	2.00
	210	0.35	1.07	1.55
2.....	183	0.88	1.58	3.20
	186	0.44	0.69	1.16
	194	0.22	0.69	0.81
3.....	170	0.45	0.57	1.06
	184	0.83	0.87	0.99
	194	0.49	0.57	0.69
4.....	162	0.63	0.49	0.58
	166	0.66	0.63	0.63
	170	0.61	0.60	0.65

Results—Comparison with Porosity

The only conclusion that can be drawn from this tabulation of results is that segregation is not an important factor in porosity. Among solders Nos. 1, 2 and 3, good and poor solders alike show

segregation to a large extent. No marked difference seems to exist, for example, between the segregation of solder No. 2, which forms non-porous joints, and solder No. 1, which is a poor solder from the standpoint of porosity. On the other hand, in solder No. 4, an extremely poor solder, segregation is so slight as to be negligible. In Fig. 7 are plotted the data for solders Nos. 1 and 4, the former showing

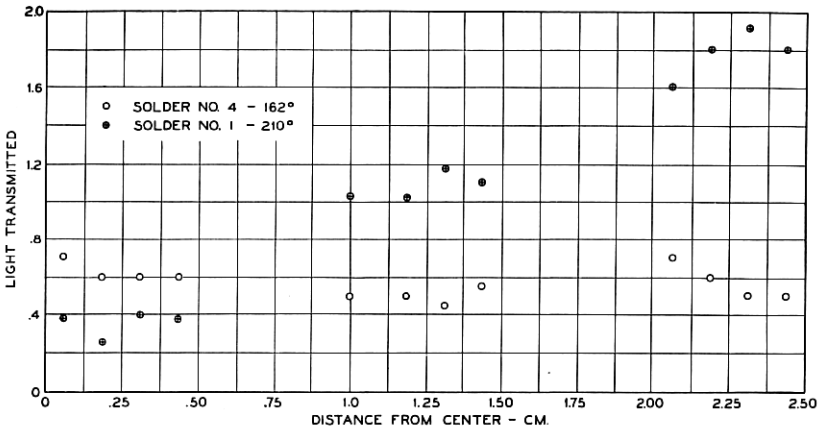


Fig. 7—Segregation measurements on two solder samples.

considerable segregation and the latter practically no segregation of solid from liquid phase.

It is interesting to note how well the segregation measurements confirm the plasticity data. Solders Nos. 1, 2, and 3, showing clearly the quasi-viscous type of flow, also show marked segregation, revealing the reluctance of the solid particles to move and their consequent piling up near the center of the sample. In solder No. 4, the flow is of the viscous type, and consequently there is no segregation. The solid phase and the liquid phase do not separate, but flow together as a viscous whole.

PARTICLE SIZE

Relation to Porosity

It was thought that in solders forming porous joints the solid phase may, at wiping temperatures, be present as particles relatively large in size, in which case the liquid must be in larger recesses than would be the case if the particles were small. The cohesion of the solder while it is being worked and while it is solidifying must depend to some extent upon the adhesion between solid and liquid. The larger the particles, the greater the distances through which the surface

forces must operate in hindering the free motion of the liquid phase. The liquid phase in a two-phase system where the particles are large should then be only loosely bound to the mass, and though there might be no gross tendency toward segregation, this liquid phase should in working be squeezed out, leading to cavity formation and consequent porosity.

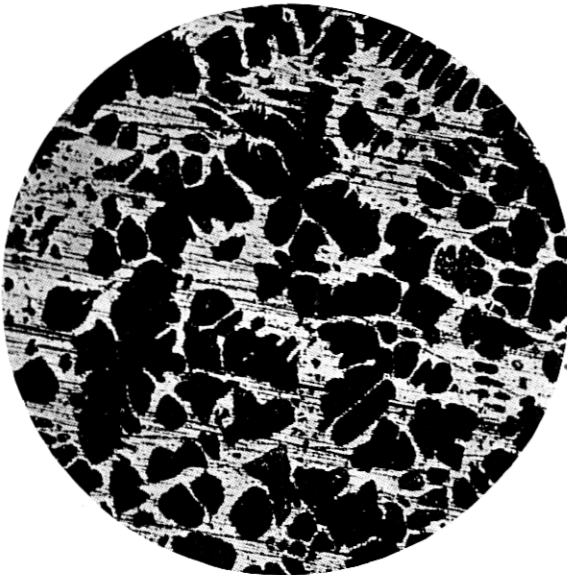
Experimental

To test this explanation of porosity two samples of solder No. 1 were quenched from 210° C. and two of solder No. 2 from 200° C., at which temperatures these solders exhibit practically the same plasticity. Though the data are too meagre to allow generalizations to be made, the results in both sets of samples were well in line with the theory. Microscopic examination showed a much coarser particle structure in solder No. 1 than in solder No. 2, as illustrated by Fig. 8. In this instance at least the solder which forms porous joints tended to form solid particles at wiping temperatures larger than those formed in the solder which is acceptable from the standpoint of porosity.

Particle Size and Porosity as Related to Wettability

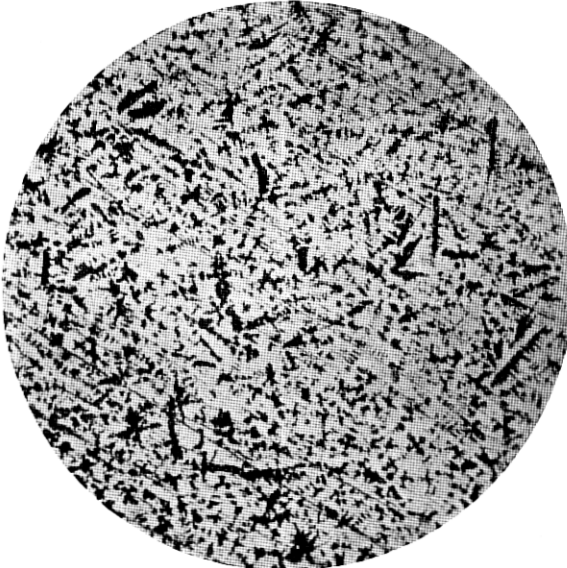
It appears that this test may have a significance beyond that just attached to it, and since it may conceivably be used again in the study of solders, it is perhaps well to point out a further explanation based on the theory of interfacial tension.

As was stated earlier in this paper, one demand upon a wiping solder is that it shall wet the cable covering readily. This is necessary if porosity is to be avoided, since areas of imperfect wetting will form tracks between the solder and the lead allowing passage of air or liquid along the interface. Further, the liquid phase of the solder must wet the solid phase of the solder; otherwise passages will exist in the body of the joint. There is some question as to whether porosity in a joint is more commonly due to lack of adherence between the sheath and the solder or whether complete air passages may exist throughout the solder itself. At any rate, there is no assurance that either type of failure does not exist. These two types of porosity are, however, very similar phenomena from the standpoint of wettability, since both the cable sheath and the solid particles of the solder are composed chiefly of lead. If the liquid phase of the solder will wet the sheath, it will also wet the solid particles of lead within the solder, and neither type of failure will be likely to occur. The problem resolves itself into one of the wettability of lead by the liquid phase of the alloy. Therefore, if it is possible to determine, at equal plasticities, the relative



LARGE
CRYSTALS

POROUS
WIPING SOLDER
65% Pb. — 35% Sn.
AIR COOLED TO 210° C.
AND QUENCHED



SMALL
CRYSTALS

NON — POROUS
WIPING SOLDER
60% Pb. — 40% Sn.
AIR COOLED TO 200° C.
AND QUENCHED

Fig. 8—The porosity of wiping solders as related to the crystal size of samples air cooled to equivalent consistencies and quenched.

adherence of liquid to solid for different solders, the relative likelihood of porous joints occurring should be thereby indicated.

Wettability depends upon interfacial tension. As pointed out by Osterhof and Bartell,¹⁰ high wetting power of a liquid for a solid means a low interfacial tension between the two, which in turn means a high adhesion tension.

Furthermore, if the interfacial tension between a liquid and a dispersed solid is high, the formation of large grains, crystals, or flocculates will take place, thus diminishing the amount of solid-liquid interface and the total free energy of the system. This has been used to account for the increased solubility of small particles in contact with a saturated solution, with the consequent growth of large crystals^{11, 12} and in paint technology to explain the formation of groups of particles or flocculates.^{13, 14} If, on the other hand, the interfacial tension is low, as for solders of high wettability, the particles have a tendency to remain small. This fact has been used to account for the high development of surface in colloidal solutions.

This would lead to the conclusions that in solder No. 1, where large solid particles exist, the liquid phase wets the lead dispersed within it and hence also the lead of the cable sheath but poorly, while in solder No. 2, exhibiting finer grain formation, the wetting power of the liquid phase for lead is high. These considerations alone would point to a conclusion which has been shown to be the case—that solder No. 1 is more likely to form porous joints than solder No. 2.

SUMMARY

An attempt has been made to correlate important qualities of wiping solders with measurements of plasticity, segregation, and particle size.

A study of six solders has shown that their deformation in the working range is in accord with the theory of quasi-viscous flow, which assumes the shearing stress to be proportional to a fractional power of the velocity gradient.

It appears that what is required of a solder, in order that it can be properly worked, is a low variation in plasticity with temperature. This allows the solder to be worked for a comparatively long period while it is losing heat to the atmosphere. This requirement appears to be satisfied for solders whose resistance to deformation differs most markedly in character from that of a viscous liquid.

¹⁰ H. J. Osterhof and F. E. Bartell, *J. Phys. Chem.*, **34**, 7 (1930).

¹¹ H. Freundlich, "Colloid and Capillary Chemistry," E. P. Dutton (1922).

¹² Willows and Hatschek, "Surface Tension and Surface Energy," P. Blakiston & Son (1919).

¹³ Bartell and Van Loo, *Ind. & Eng. Chem.*, **17**, 1051 (1925).

¹⁴ Wm. Green, *Ind. & Eng. Chem.*, **15**, 122 (1923).

Determinations of the rate of compression of solders at wiping temperatures between parallel plates have been found to conform to the equation:

$$\frac{dh}{dt} = kh^b,$$

in which dh/dt is the rate of compression, h the sample height, and k and b are constants, the latter depending only on the character of the material. For viscous materials $b = 5.0$; the larger the value of b , apparently, the more does the flow differ from that of a viscous liquid. Solders having large values of b (15–25) have low temperature gradients of plasticity and good workability, in agreement with the conclusions noted above.

It has been shown that the plasticity cannot be predicted from the solid-liquid ratio.

Evidence is presented that segregation is not responsible for the porosity of wiped joints, and that this defect may be related to the particle size of the solid phase at wiping temperatures. The relation of particle size to cavity formation and to the cohesion and wetting power of the solder is discussed.

APPENDIX

As stated in the body of this paper, a series of runs were made on solder No. 2 at 183° C. to determine how closely the results of such tests agree with the theoretical expression for quasi-viscous flow given as Equation (4) above. Only five test runs were made, the minimum sufficient to indicate the existence of such agreement. The sample volumes and loads used in these runs are listed in Table IV. For each

TABLE IV

Run No.	V c.c.	W kgs.	b	σ_b	$\log k$	S	$\log k'$	S'	$\Delta \log k'$
1.....	5.45	13.6	16.10	4.32	-34.36	0.0384	-34.472	0.0352	0.073
2.....	7.34	13.6	17.73	3.99	-37.58	0.0351	-35.556	0.0473	0.122
3.....	11.01	13.6	15.68	1.85	-35.53	0.0225	-36.577	0.0257	0.067
4.....	7.30	20.8	15.76	1.43	-34.38	0.0131	-35.209	0.01553	0.098
5.....	7.33	27.2	15.51	2.83	-33.51	0.0249	-34.853	0.0286	0.078

$$\bar{b} = 16.156$$

$$\sigma'_b = 0.906$$

$$a = 1.656$$

$$c = 6.875$$

$$\log K = -31.359$$

run there was prepared a plot of sample height (h) vs. time (t), and values of dh/dt were determined from the slopes of tangents drawn as

shown in Fig. 1. There were thus obtained for each run a set of six or seven pairs of values of $\log dh/dt$ vs. $\log h$.

The first question to be determined is whether for any run these pairs of values agree with a relation of the form of Equation 1, which can be written:

$$\log \frac{dh}{dt} = \log k + b \log h. \tag{5}$$

As sample height readings appear to be reproducible in such tests to within about one per cent, the standard deviation of values of $\log h$ about their correct values may be estimated as rather less than 0.004 ($\log 1.01$). The time readings being more accurate, values of $\log dh/dt$ should vary with a standard deviation of like magnitude. If the data can be fitted by an equation of the form of Equation 5, estimates of k and b can be obtained by minimizing the sum of the squares of the deviations of the experimental points from the straight line, these deviations being measured along normals to the line. As for these data b is large, these normal deviations are nearly equal to their horizontal components, the deviations of the observed from the calculated values of $\log h$, and hence the sum of the squares of the latter were minimized. Writing X_i for values of $\log h$ and Y_i for corresponding values of $\log dh/dt$, the following computations were carried out for each run (n being the number of pairs of values employed in each case):

$$\begin{aligned} \bar{X} &= \frac{\sum_{i=1}^n X_i}{n}, & \bar{Y} &= \frac{\sum_{i=1}^n Y_i}{n}, \\ \sigma_x^2 &= \frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n}, & \sigma_y^2 &= \frac{\sum_{i=1}^n (Y_i - \bar{Y})^2}{n}, \\ b &= \frac{n \sigma_y^2}{\sum_{i=1}^n X_i Y_i - n \bar{X} \bar{Y}}, & \log k &= \bar{Y} - b \bar{X}, \\ S^2 &= \frac{\sum_{i=1}^n (Y_i - \log k - b X_i)^2}{n - 2}. \end{aligned}$$

Values of b , $\log k$, and S thus determined are included in Table IV. The quantity S is an estimate of the standard deviation of the observed

from the calculated values of $\log dh/dt$ evaluated as recommended by Fisher,¹⁶ page 118. To determine in each case whether these deviations are significant, they may be compared with those that might be expected on the basis of the estimated precision of measurement. As the value of b is approximately 16 in each case, an error of 0.004 in $\log h$ corresponds to an error of 0.064 in $\log dh/dt$. The values of S computed are all smaller than this amount, indicating that the differences between observed values of $\log dh/dt$ and those calculated from Equation 1 are due to experimental variations.

The next question to be determined is whether the differences observed in the values of b given by the different runs are significant. In Table IV is included the mean value \bar{b} of the values of b , together with the estimated standard deviation of the individual values of b from their true mean, taken as given by:

$$\sigma_b' = \sqrt{\frac{\sum (b - \bar{b})^2}{n - 1}}.$$

This estimate of the standard deviation of the actual values of b may be compared with estimates of the standard deviation of b made for each run on the basis of the variability of the data. An expression for such an estimate is given by Fisher (loc. cit.) as:

$$\sigma_b^2 = \frac{nS^2}{\sigma_x^2}.$$

Values of σ_b as given by this last expression are included in Table IV. These are larger than the value (0.906) of σ_b' , computed as described, and it is therefore evident that the data are consistent with the hypothesis that b is constant throughout the series of runs.

To obtain fairer estimates of $\log k$ for the subsequent computation, the mean value of b , \bar{b} , was taken as giving the slope of the straight line of Equation 5. On this basis the values of $\log k$ are given by:

$$\log k' = \bar{Y} - \bar{b}\bar{X}.$$

While the values of S are given by:

$$S'^2 = \frac{\sum_{i=1}^n (Y_i - \log k' - \bar{b}X_i)^2}{n - 1}.$$

Values of $\log k'$ and S' are given in Table IV. The next step in the computation is to determine if the values of $\log k$ thus determined

¹⁶ R. A. Fisher, "Statistical Methods for Research Workers," London (1925).

vary significantly from those given by Equation 2 above, or by:

$$\log k' = \log K + a \log W - c \log V. \tag{6}$$

For this purpose there were determined values of $\log K$, a and c for which the sum of the squares of the differences of observed and calculated values of $\log k'$ are a minimum, the components of deviation due to variations in values of $\log W$ and $\log V$ being neglected, as these are known to a higher order of accuracy than are values of $\log k'$. Following the usual procedure for calculating partial regression coefficients, the following computations were performed, writing Z_i , Y_i , and X_i for corresponding values of $\log k'$, $\log W$ and $\log V$:

$$\begin{aligned} \bar{Z} &= \frac{\sum_{i=1}^n Z_i}{n}, & \bar{Y} &= \frac{\sum_{i=1}^n Y_i}{n}, & \bar{X} &= \frac{\sum_{i=1}^n X_i}{n}, \\ \sigma_Z^2 &= \frac{\sum_{i=1}^n (Z_i - \bar{Z})^2}{n}, & \sigma_Y^2 &= \frac{\sum_{i=1}^n (Y_i - \bar{Y})^2}{n}, & \sigma_X^2 &= \frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n}, \\ \sum xy &= \sum_{i=1}^n X_i Y_i - n \bar{X} \bar{Y}, & \sum yz &= \sum_{i=1}^n Y_i Z_i - n \bar{Y} \bar{Z}, \\ & & \sum zx &= \sum_{i=1}^n Z_i X_i - n \bar{Z} \bar{X}, \\ a &= \frac{n \sigma_x^2 \sum yz - \sum xy \cdot \sum xz}{n^2 \sigma_x^2 \sigma_y^2 - (\sum xy)^2}, & -c &= \frac{n \sigma_y^2 \sum xz - \sum xy \cdot \sum yz}{n^2 \sigma_x^2 \sigma_y^2 - (\sum xy)^2}, \\ \log K &= \bar{Z} - a \bar{Y} + c \bar{X}. \end{aligned}$$

The values of a , c , and $\log K$ thus obtained are included in Table IV, together with values headed $\Delta \log k'$, which are the differences between the values of $\log k'$ listed in Table IV and those calculated from Equation 6, using the listed values a , c , and $\log K$. To determine whether these differences are significant or not, the probability of obtaining a value in error to that extent may be calculated for each run from the value (S') of the standard deviation of $\log k'$ estimated by the method given by Fisher (loc. cit.). These probabilities are evaluated from Table IV of the text cited, taking n as $n' - 3$, where n' is the number of pairs of values of $\log dh/dt$ and $\log h$ used to evaluate $\log k'$, and taking t as:

$$t = \frac{\Delta \log k' \sqrt{n'}}{S'}$$

The values of t thus computed range from 5.4 to 16.7 and correspond in every case to a probability less than 0.01, so that not one of the

actual values of $\log k'$ should be experimentally in error to an extent sufficient to account for its deviation from the value given by Equation 6. Hence Equation 2, is at best only an approximation to a correct expression for dh/dt .

Of course, Equation 2 is actually quite a fair approximation to an expression for dh/dt , as is evident in comparing the differences $\Delta \log k'$ with the differences among the values of $\log k'$ themselves. In fact, if values of $\log k'$ are plotted against $\log W$ for a constant value of V , or against $\log V$ for a constant value of W , quite good straight lines are obtained, and the inaccuracy of the approximation can only be brought out by an analysis such as is here given. Whether this inaccuracy is due to the approximations employed in the theoretical development of Equation 4, or to an error in the basic assumption that $\tau = [dv/dx]^{1/n}$, cannot, of course, be determined. It is, however, of interest to see if the values of a and c are related to that of b in the manner required by Equation 4. For $b = 16.156$ (the value of \bar{b} observed), Equation 4 requires that $a = 5.462$ and $c = 8.693$. The observed values of a and c are 1.656 and 6.875 respectively. It remains to determine if these differences may be accidental, provided the values of $\log k'$ differ from those given by Equation 6 as greatly as observed. Following Fisher (page 133), the probability of a divergence between observed and calculated values of c of $c_1 - c_2$ is given by entering Table IV of the text with $n = n' - 3$, where n' is the number of cases (5), and with t given by:

$$t = \frac{C_1 - C_2}{\sqrt{\frac{[Z - (\bar{Z} + a\bar{Y} - c\bar{X})]^2}{n - 3} \cdot \frac{n\sigma_y^2}{n^2\sigma_x^2\sigma_y^2 - (\sum xy)^2}}} = 3.58.$$

This corresponds to a probability between 0.05 and 0.10, which indicates that the divergence may be due to chance, though it is more likely to represent a real difference. Similarly the probability of obtaining the observed difference $a_1 - a_2$ is given from the table by entering with $n = 2$ and with t given by:

$$t = \frac{a_1 - a_2}{\sqrt{\frac{[Z - (\bar{Z} + a\bar{Y} - c\bar{X})]^2}{n - 3} \cdot \frac{n\sigma_x^2}{n^2\sigma_x^2\sigma_y^2 - (\sum xy)^2}}} = 5.85.$$

This corresponds to a probability between 0.02 and 0.05, which suggests more strongly than does the other case that the divergence is real. For so few observations, however, the distribution theory on which Fisher's method is based cannot give a definite indication when

the probabilities lie so close to the arbitrary dividing line (0.05) between likely and unlikely results. The analysis therefore leaves open the question as to whether the theoretical relation given by Equation 4 between a , b and c is valid within the limits of variability imposed by the approximate nature of any relation of the form of Equation 2. That any equation of this form is only approximately in agreement with these data is conclusively shown by the above analysis.