

XX. *On the Velocity of Solidification and Viscosity of Supercooled Liquids.* By HAROLD A. WILSON, B.A. (Camb.), D.Sc. (Lond.), M.Sc. (Vict.), 1851 Exhibition Scholar, Allen Scholar, Cambridge University*.

IN the following paper an account is given of a series of experiments, the object of which was to obtain information on the influence of the viscosity of a supercooled liquid on its rate of solidification. When solidification is started in a supercooled liquid, rays of solid grow in the liquid with a definite velocity the relation of which to the initial supercooling has been determined † for a number of substances, *e. g.* phosphorus and benzophenone. In considering the nature of the observed relation between the velocity and the supercooling, it is important to take into account the production of heat which accompanies the solidification, and which must raise the temperature of the surface at which the solidification takes place; so that the observed relation may differ greatly from the relation between the velocity and the temperature of the solidifying surface.

In a previous paper "On Velocity of Solidification" ‡ I have shown that the general character of the relation observed between the velocity of solidification and the supercooling of the liquid can be explained in detail by supposing the solidification to be due to the difference between the internal pressures in the liquid and solid, and that the molecules at the surface of separation between the solid and liquid are urged from the liquid into the solid by this difference in the internal pressures. Using the method given by Van't Hoff for calculating the osmotic pressure of a salt in solution from the depression of the vapour-pressure, and making certain assumptions described in detail in the paper just referred to, the following formula for the velocity was obtained:—

$$v = \frac{F}{A\alpha} \cdot \frac{\theta_0 - \theta}{\theta_0},$$

where v is the velocity of solidification, F the latent heat of fusion of one gram of the solid, A the force required to give unit velocity to one gram of the liquid diffusing through itself, α the thickness of the layer of molecules at the sur-

* Communicated by the Author.

† Gernez, *Journ. de Phys.* [2] ii. p. 159. Friedländer & G. Tammann, *Zeitschr. f. Phys. Chem.* xxiii. p. 326, and xxiv. p. 152.

‡ Proc. Camb. Phil. Soc. vol. x. pt. 1.

face of separation of the liquid and solid in which the fall of pressure takes place, θ_0 the melting-point on the absolute scale, and θ the actual temperature at the surface of separation.

If we regard F and α as constants and A as being proportional to the viscosity of the liquid, we can write the above formula thus :

$$v = C \frac{s}{V},$$

where C is a constant, $s = \theta_0 - \theta$ the actual supercooling, and V is the viscosity of the liquid.

Since V increases as the temperature falls, v may attain a maximum value and then fall when s is increased.

The experiments described in this paper were undertaken with the object of testing the formula $v = C \frac{s}{V}$; and they show that the main features at any rate of the observed relation between the velocity and temperature can be deduced from the results for the viscosity by means of this formula. In fact, when the constant C is so chosen as to make the maximum value of $C \frac{s}{V}$ equal to the maximum value of the velocity, then the values of $C \frac{s}{V}$ agree fairly well with the observed values of the velocity.

To find the extent to which the temperature of the solidifying surface, or rather that of the tips of the growing rays of solid, is raised above the original temperature of the liquid, experiments were made in which a thermocouple was immersed in the liquid, and the change in its temperature observed as the boundary between the solid and liquid passed it. The substance first used was salol, which was chosen because it solidifies very slowly (maximum velocity about 4 millimetres per minute), so that the thermocouple has a chance of taking up the temperature of the surface of separation.

The salol was contained in a glass U-tube which was immersed in a water-bath at constant temperature, and the thermocouple was put down one of the limbs of the U-tube. The couple used was made from iron and nickel wires each 0.2 millim. in diameter, which were twisted together for about 2 millims. and kept apart by a thin capillary of glass round the iron wire. The iron and nickel wires dipped into small mercury cups kept in the same water-bath, from which

copper wires led to a very dead-beat mirror-galvanometer read by a telescope and scale. A deflexion of about 3 millim. divisions was obtained for a difference of temperature of one degree between the couple and the mercury cups, so that $\frac{1}{5}$ of a degree could be measured easily.

The salol was first melted by means of hot water, and then the U-tube was fixed in the bath and the couple put halfway down one limb. When the salol had taken up the temperature of the bath, solidification was started in the other limb, and the galvanometer observed as the surface of separation passed the couple. A millimetre-scale was fixed to the U-tube, so that the temperature of the couple and its position with respect to the surface of separation could be observed simultaneously. The following series of observations were obtained in one experiment:—

Diameter of tubing, 0.5 centim.

Temperature of bath, 31° 5 C.

Melting-point of the salol, 41° C.

Distance of the Couple from the mms.	Solid.	Temperature-Difference indicated by the Couple.
5.6	0
5.1	0
4.7	0.2
2.8	0.9
2.3	1.2
1.4	1.5
1.0	1.9
0.5	2.4
0.4	3.0
0.0	3.3
-0.8	2.7
-2.0	0.5

The velocity of the boundary in this experiment was 1.3 millim. per minute. The maximum temperature was always indicated in the time during which the couple was partly in the solid and partly in the liquid. The twisted wires formed a couple about 0.4 millim. in diameter; so that in the experiment just described this time was about 18 seconds. The following table gives the maximum rise of temperature observed with the same tube at several temperatures.

Temperature of Bath.	Maximum Rise observed.	Temperature at which Solidification occurred.	Corresponding Velocity of Solidification.
31.5	3.3	34.8	mms./min. 1.3
27.5	5.6	33.1	2.4
22.0	9.0	31.0	3.4
17.0	8.9	25.9	3.9
11.5	9.0	20.5	4.1

The following table gives the results obtained with a tube 0.2 centim. internal diameter.

Temperature of Bath.	Maximum Rise observed.	Temperature at which Solidification occurred.	Corresponding Velocity of Solidification.
36.0	0.6	36.6	mms./min. 0.4
32.5	1.6	34.1	1.8
31.0	2.2	33.2	2.3
25.3	2.8	28.1	3.8
21.0	3.4	24.4	4.0
16.7	3.6	20.3	4.1
11.3	3.8	15.1	4.1

The last column in each of the above two tables contains the velocities of solidification in the same tubes obtained by interpolation from observations on the velocity at a number of temperatures. The velocity was determined by measuring the time taken by the boundary to pass between two marks on the tube at a known distance apart. The following results were obtained with the same two tubes:—

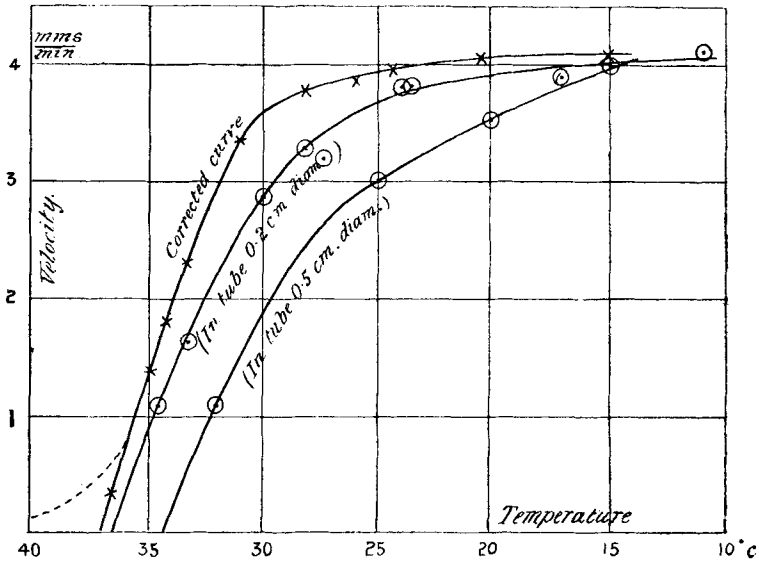
Tube 0.5 centim. in diameter.

Temperature of Bath.	Velocity of Solidification.
°	mms./min.
32.0	1.10
25.0	3.02
20.0	3.55
15.0	4.00

Tube 0.2 centim. in diameter.

Temperature of Bath.	Velocity of Solidification.
	mms./min.
34.3	1.10
33.0	1.62
30.0	2.88
28.0	3.30
27.0	3.23
24.0	3.87
23.5	3.88
17.0	3.93
11.5	4.13

Fig. 1.—Velocity of Solidification of Salol.



These results are shown graphically in fig. 1. It will be observed that the velocities are not the same at the same temperatures in the two tubes; but when the correction indicated by the thermocouple is applied, the two curves become approximately identical. The wider tube had thicker walls than the narrower one, which of course would render the escape of the heat developed more difficult in the wider tube, which accounts for the greater rise of temperature found in it.

The effect on the velocity of surrounding the tube by a

wider glass tube forming an air-jacket was tried. This was found to diminish the velocity considerably, as we should expect owing to the increased difficulty with which the heat developed could escape. Thus with the water-bath at 32° the velocity with the additional tube was $0.88 \frac{\text{mm.}}{\text{min.}}$, and without the additional tube it was $1.1 \frac{\text{mms.}}{\text{min.}}$.

To test the validity of the formula $v = C \frac{s}{\sqrt{V}}$, the viscosity of supercooled salol was measured at a number of temperatures. The apparatus was of the ordinary form, consisting of two small glass bulbs connected by a capillary and bent round into a U-shaped tube. The time required by the meniscus of the liquid to pass between two marks, one above and one below the upper bulb, was determined whilst the apparatus was fixed in a water-bath at a known constant temperature. The capacity of the upper bulb was about 2 cub. cent., and the time for water at 15° C. was 24.5 seconds.

The open ends of the U-tube were connected by india-rubber tubes to bulbs containing calcium chloride to prevent moisture getting to the liquid. When the liquid began to solidify, it was melted by putting the tube in hot water. The following table gives the results obtained for the viscosity of salol.

Salol.

Melting-point, 41° C.

Density 1.195 at 35° C.

Temperature.	Time.	Viscosity. (Water at 15°=1.)
42.0	149.3	7.27
35.9	196.5	9.57
29.0	278.5	13.57
25.0	350.0	17.05
19.5	519.2	25.29
15.0	649.0	31.60

These results are shown graphically in fig. 3.

The formula $v = C \frac{s}{\sqrt{V}}$ indicates that the velocity should increase proportionally to the supercooling when it is small. Now the relation observed between the velocity and super-

cooling usually shows a very small rate of increase of velocity when the supercooling is small. This is shown in fig. 1, where the velocity-curve produced cuts the axis of temperature at 37° , whilst the melting-point of the salol was about $41^{\circ}\cdot 0$. Still some indications of partial melting occurred at about 37° ; and it is very probable that if the substance were quite pure, then the very small rate of increase of the velocity near the melting-point would not occur. Tammann (*loc cit.*) has shown that purifying a substance always diminishes this region of small velocity; and consequently, for the purpose of testing the formula $v = C \frac{s}{V}$, I have measured the supercooling from the point ($37^{\circ}\cdot 0$) at which the velocity-curve shown in fig. 1 cuts the temperature-axis.

To get the value of C in the formula $v = C \frac{s}{V}$ the values of the velocity (v) and viscosity (V) were taken at 22° , at which temperature s is 15° ; hence $C = \frac{4\cdot 1 \times 21\cdot 0}{15} = 5\cdot 74$.

The following table shows the results obtained, using the formula $v = 5\cdot 74 \frac{s}{V}$ and values of V taken from the curve for the viscosity of salol.

Temp.	s .	V .	v $= 5\cdot 74 \frac{s}{V}$	v . (Found.)
35°	2	10·0	1·15	1·25
33	4	10·7	2·14	2·5
31	6	12·0	2·90	3·2
29	8	13·5	3·40	3·7
27	10	15·0	3·82	3·9
25	12	17·0	4·05	4·0
21	16	22·5	4·08	4·1
19	18	25·0	4·13	4·1
15	22	31·6	4·00	4·1

The agreement between the found and calculated values of v is sufficiently good. The independence of the velocity and the temperature from 15° to 25° thus appears to be due in this case to the viscosity being approximately proportional to the supercooling between these limits of temperature.

The formula $v = C \frac{s}{V}$ thus represents the variation of the

velocity with the temperature at which it takes place in a very satisfactory manner in the case of salol.

In the case of substances having greater velocities of solidification than salol, it is not easy to determine the rise in temperature during solidification. I have made measurements of the viscosity and velocity of solidification of supercooled salol, benzophenone, benzoic anhydride, and azobenzol, for which measurements of the velocity have also been made by Friedländer and Tammann (*loc. cit.*), and my results for the velocity do not differ much from those given by them. Benzoic anhydride has a maximum velocity of about $35 \frac{\text{mms.}}{\text{min.}}$; so that the thermocouple would only be in the boundary for 0.6 sec., which is probably not long enough to enable it to take up the temperature at the boundary.

Another difficulty was that the galvanometer available had rather a long period of swing, so that it could not be used for measuring so sudden a rise of temperature. An attempt was made to increase the time during which the couple was in the boundary, by moving it along with a velocity nearly equal to the velocity of the boundary; and an apparatus was made which automatically did this. Unfortunately, however, the motion of the couple in the liquid nearly always caused it to solidify, and the couple became fixed in the solid. I believe that this could be prevented by taking care not to allow the wires from the couple to carry any of the liquid into the cold air above the bath, and by heating the couple with the liquid for a long time; but I am not able at present to devote any more time to these experiments, and shall therefore simply use the results obtained to test the formula $v = C \frac{s}{V}$ without correcting for the rise in temperature during the solidification.

The following Tables give the results obtained with benzoic anhydride. The velocity was measured between two marks 10 cms. apart on a tube 0.3 cm. in diameter. The apparatus already described was used for the viscosity determinations.

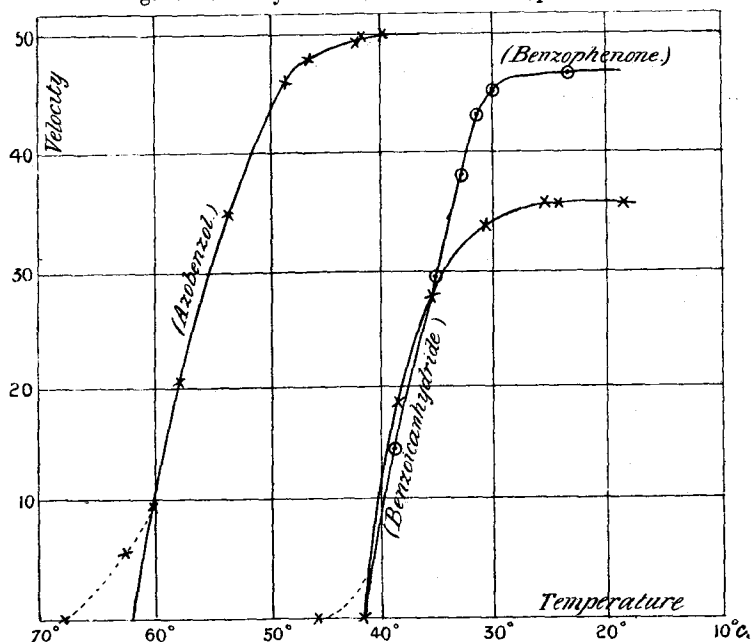
Benzoic anhydride.

Melting-point, 42° C.

Density at 38° C., 1.188.

Velocity of Solidification.		Viscosity. (Water at 15°=1.)		
Temp.	Velocity.	Temp.	Time.	Viscosity.
	mms./min.		secs.	
38.0	18.8	39.7	287.5	13.97
35.0	29.1	34.0	370	17.84
30.6	33.6	33.3	382	18.57
26.5	35.2	27.3	513	24.92
24.75	34.9	20.65	757	36.79
18.75	34.9	18.5	880	42.77
		12.1	1384	67.25

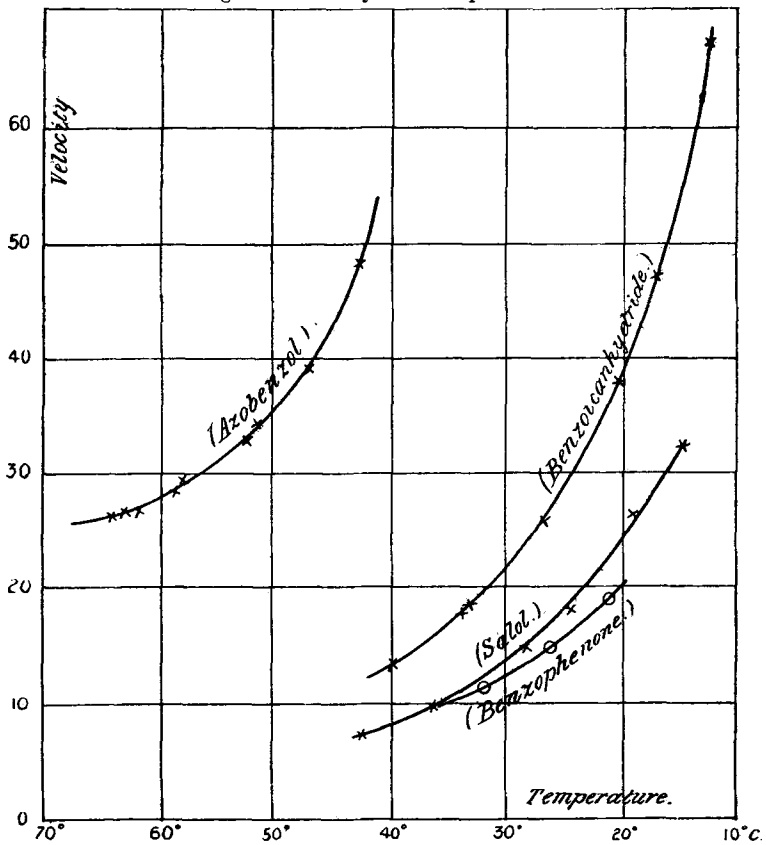
Fig. 2.—Velocity of Solidification and Temperature.



These results are shown in figs. 2 and 3. Calculating in the same way as before, we get $\bar{C}=60$, which gives the following results:—

Temp.	s.	V.	$\frac{v.}{(=C \frac{s}{V})}$.	$\frac{v.}{(Found.)}$
			mms./min.	mms./min.
38	4	15.0	16.2	18.0
34	8	17.7	27.2	30.5
30	12	22.0	32.8	34.0
26	16	27.0	35.6	35.0
22	20	34.0	35.3	35.0
18	24	43.1	33.8	35.0
12	30	67.5	26.7

Fig. 3.—Viscosity and Temperature.



The agreement between the found and calculated value of v is about as good as it was with salol, although the

rise in temperature due to the solidification has not been allowed for. It may be that the rise in temperature is less when the velocity of solidification is greater; and so neglecting the rise may not make much difference. The calculated value of v at 18° C. is smaller than at 22° C., so that at 18° C. the supercooling is greater than that for which v is a maximum. Hence the temperature of the solidifying surface is probably* raised by the heat developed to the temperature at which v is a maximum; so that when the bath is below this temperature the actual temperature at which the solidification takes place remains constant, consequently observations on the velocity cannot really be made at any lower temperature unless the temperature is so low that the latent heat of solidification is not enough to raise the temperature up to that at which the velocity is a maximum. Hence the calculated values of the velocity will not agree with the uncorrected values found apparently below the temperature at which the velocity is a maximum except so long as the calculated velocity also remains practically constant at the maximum value.

The following Tables give the results obtained with benzophenone.

Benzophenone.

Melting-point, $46^{\circ}\cdot5$ C.

Density at 31° C., 1·099.

Velocity of Solidification.		Viscosity. (Water at $15^{\circ}=1$.)		
Temp.	Velocity.	Temp.	Time.	Viscosity.
	mms./min.	$^{\circ}$	secs.	
38·3	15·0	32·93	241·0	10·80
34·7	31·9	27·10	319·5	14·33
33·0	37·8	21·9	410·5	18·41
32·0	43·0			
30·0	45·9			
24·0	46·4			

These results are shown graphically in figs. 2 and 3. Calculating in the same way as before, we get $C=44\cdot1$, which gives the following results:—

* See paper "On Velocity of Solidification," *loc. cit.*

Temp.	s.	V.	$\frac{v.}{(=C \frac{s}{V})}$	$\frac{v.}{(Found.)}$
38	4	9.0	19.6	15.0
34	8	10.4	33.8	34.0
32	10	11.1	39.8	43.0
30	12	12.4	42.7	45.9
28	14	13.6	45.5	46.0
26	16	15.1	46.7	46.4
24	18	16.9	47.0	46.4
22	20	19.3	45.6	46.4

The following are the results obtained with azobenzol, which are also shown graphically in figs. 2 and 3:—

Azobenzol.

Melting-point, 67° 5 C.

Density at 50° C., 1.038.

Velocity of Solidification.		Viscosity. (Water at 15°=1.)		
Temp.	Velocity.	Temp.	Time.	Viscosity.
	mms./min.		secs.	
62.0	57.1	65.1	60.2	2.56
59.7	88.2	63.7	61.5	2.61
57.1	207.0	61.9	62.1	2.64
53.4	345	58.5	65.5	2.78
48.8	465	57.8	66.6	2.83
45.5	484	57.5	68.0	2.89
42.0	492	52.8	75.0	3.19
41.4	500	51.6	79.0	3.36
39.5	500	47.0	92.1	3.92
.....	43.1	111.0	4.70

Calculating in the same way as before, we get C=125, which gives the following results:—

Temp.	s.	V.	$\frac{v.}{(=C \frac{s}{V})}$	$\frac{v.}{(Found.)}$
60	2	2.72	92	90
58	4	2.82	177	170
56	6	2.94	255	250
54	8	3.10	322	320
52	10	3.30	379	390
50	12	3.52	426	445
48	14	3.80	460	470
46	16	4.13	485	483
44	18	4.52	498	490
42	20	5.00	500	495

It thus appears that the formula $v = C \frac{s}{\sqrt{\eta}}$ represents the variation of v with s sufficiently well to justify the conclusion that the velocity is largely determined by the viscosity in the way indicated by the formula.

Two main causes, to which I have already referred, probably account for the discrepancies between the values of $C \frac{s}{\sqrt{\eta}}$ and the velocities observed. The first cause, namely, the rise of temperature due to the production of heat accompanying the solidification, does not affect the comparison of the calculated and observed velocities in the case of salol, for in this case it was measured and allowed for; but with the other three bodies investigated the temperatures at which the velocities are measured are too low, owing to this effect. If the correction for this effect were made, it would probably raise the point at which the straight part of the velocity-curve when produced cuts the temperature-axis, so that measuring s from this point probably partly eliminates the error due to this cause.

The other cause, namely, the presence of impurities in the substance, probably accounts for the small velocities observed near the melting-point, which I have not attempted to represent by the formula, and which occur with three out of the four substances investigated. When impurities are present, solidification near the melting-point is more correctly described as crystallization from a strong solution, and must evidently depend on the rates of diffusion of the substance and impurities in each other, for as the pure substance separates out the impurities collect round it; and so it is easy to see that the rate of solidification may be greatly affected by small amounts of impurities quite insufficient to have a corresponding influence on the viscosity of the substance. That purifying the material is able to diminish greatly the range of temperature over which the velocity increases very slowly with the supercooling has been shown by Friedländer and Tammann (*loc. cit.*), so that it seems reasonable to suppose that with pure substances the velocity would be at first proportional to the supercooling, as the formula $C \frac{s}{\sqrt{\eta}}$ indicates, and as is approximately the case with the benzoic anhydride I used.

I think, therefore, that the above results render it probable that the velocity of solidification of a pure substance varies directly as the actual supercooling at which the solidification occurs, and inversely as the viscosity of the liquid.

Wilmersdorf, Berlin,
Feb. 15, 1900.