the solutions were not, it must be confessed, sufficiently delicate for so dilute solutions. Yet as has been stated, they will at least show the relative strength of the solutions.

The conclusions that we have here a case of small changes in surface tension of the liquid which changes also change in sign in the case of alkali at very feeble concentration, seemed at first not to be in accord with measurements of other properties of such solutions, nor were there indications of such co-ordinations in the published work on surface tension so far as we know. One exception was found, however, and this adds interest to these experiments. Bliss describes experiments by which he studied the forces between particles in liquids. In these experiments he observed the changes in the Newton rings, produced by very light pieces of flat microscope-specimen cover-glasses which were supported on the convex surface of a large lens under water. These Newton rings served to measure the distance between the flat and the convex glass surfaces, in terms of wave-lengths of light. He noted that when caustic potash solution was added to the water covering the glass surfaces, very marked changes were produced in these rings and he writes "A trace of KOH less than 0.0007 gm. per cc. increases the layer between the glass surfaces, excess beyond this trace causes it to fall back again."

It is very probable that the effect noted by Bliss is intimately connected with the above described phenomona of increased stability of colloids, due to traces of alkali. Our own experiments as well as those described by Bliss, were not carried out with a high degree of quantitative accuracy. It is not impossible that the alkali concentration corresponding to maximum stability for different suspensions or colloids is really the same in each case and that the differences which our analyses show are due to error of some sort. For this reason and in the hope that some one will be tempted to carry on this work it was thought worth while to publish this paper.

RESEARCH LABORATORY GENERAL ELECTRIC CO.,
    SCHENECTADY, N. Y.

FURTHER STUDIES OF SUPERCOOLED LIQUIDS.

BY S. W. YOUNG AND W. E. BURKE

In a number of previous papers[2] it has been pointed out that crystallization and solidification from a supercooled liquid is very considerably influenced by the previous treatment to which the liquid has been subjected, especially by the temperature to which it has been heated and the length of time which it has been maintained at a given temperature. All the results heretofore published have been based upon observations on the

[1] Phys. Rev. 1895, 241, 273.

[2] Young and Burke. This Journal. 28, 315. and references there cited.

various hydrates of sodium thiosulphate. The investigations described in this paper were taken up in order to confirm these results, if possible, with other substances. and to subject these phenomena in general to a more thorough study.

A series of preliminary experiments of very considerable extent. but made with rather crude apparatus, was carried out in this laboratory by Mr. Frank C. Winter, who investigated the conduct of salol. thymol, p-nitrotoluene and diphenylamine. In his experiments. the substances contained in small. sealed tubes were heated for definite periods of time to temperatures respectively ten. twenty and thirty degrees above the melting points. and then transferred to other baths. which were maintained at temperatures respectively five. ten. fifteen, etc., degrees below the melting points. During this step·wise cooling. each set of tubes was held at each temperature for thirty minutes and then transferred to the next cooler bath. A count was taken of the number of tubes which had solidified at each temperature.

The results showed that the solidification of each of these substances was greatly influenced by the previous treatment. and in such a way that long heating and heating to higher temperatures both acted to increase the tendency of the substances to remain in the supercooled state. which is exactly what had been observed with the sodium thiosulphates. A few rough experiments with phosphorus showed the same phenomena.

Winter also investigated the influence of the size of the tubes, and found it to be of practically no influence for tubes between two and eight mm. internal diameter ; on the other hand. tubes much less than two mm. diameter showed greater tendency to supercooling.

As a result of Winter's experience. it was decided to choose a single substance and to investigate this in the most thoroughgoing manner pos·sible. For this purpose p-nitrotoluene was chosen. as its melting point lies at a convenient temperature. and especially as it does not supercool much below 25° and therefore does not demand low temperature baths. the maintenance of which would have added great difficulty to the investigation. The preparation used was a chemically pure product from Kahlbaum. and in order to render this perfectly uniform, all that was to be used in the investigation was melted up at one time and thoroughly stirred. The tubes were all filled from this at one time. and sealed as rapidly as possible.

The tubes were all made from one lot of glass, and were about six mm. internal diameter. The tubes. after being cut to length and sealed at one end, were immersed for several days in chromic acid cleaning mix·ture. They were then thoroughly washed in distilled water and dried in an air-bath. after which they were kept in desiccators until filled and

finally sealed up. About three hundred tubes were used in the investigation, and of these one hundred were evacuated with a mercury pump.

In order that the individual conduct of each tube might be followed through a long series of experiments, the following tube-holder was devised : A strip of thin copper foil, about one inch wide, was split longitudinally into three strands, an inch at each end being left intact. Twenty-five tubes were then taken, and fixed in this strip by weaving in and out of the three strands. Small clasps were then placed at each end, and the strands were drawn tight and held securely by the clamps. Four such holders were placed in each of the two thermostats used, being fastened to arms connected with the shaft of the thermostat. When the shaft revolved, each of the holders with its twenty-five tubes was successively brought into view, which made possible observations on one hundred tubes at a time, in such a way that the conduct of each individual tube could be followed. With the two thermostats, two hundred tubes were always under study.

The thermostats used were the same as in the previous investiga· tions.[1] For this investigation, devices for rapidly changing the temperature were added. A coil of copper tubing, perforated with small holes, was placed in the bottom of the tanks ; for heating, live steam was forced through this coil, while for cooling ice-water was used ; a clutch was arranged, whereby the speed of the rotation of the shaft, with its fans, could be increased to about one hundred and thirty revolutions per minute, thus avoiding any noticeable local chilling or heating ; convenient heaters for maintaining the elevated temperatures necessary were made from two pieces of thin copper foil, separated from one another by six or eight thicknesses of toweling and rolled up into the form of a cylinder ; these were made the terminals of the 110 volt alternating current, the distilled water acting as the conductor. Such heaters are the most compact that we have been able to devise, and are fairly durable as well as easy to replace.

The experiments were carried out in the following manner : The carriers with the tubes being in place and the thermostat tank filled with water, the high speed clutch was thrown in and live steam introduced through the coil until the desired temperature was reached, time was then taken and the low speed clutch thrown in, and the apparatus allowed to run at constant temperature for the desired length of time. At the end of the period of heating, the electric heater was disconnected, the high speed clutch again thrown in, and ice-water introduced through the perforated coil ; when the temperature had fallen to the melting point of the p-nitrotoluene ($51°.2$), a stop-watch was started, the cooling being continued until the temperature had fallen five degrees below the melting point,

[1] Loc. cit.

namely to $46°.2$. The apparatus was then allowed to run on the low speed and at the latter temperature until ten minutes from the starting of the watch had elapsed ; at the end of eight minutes the work of taking the tally of the tubes which had solidified was begun, the remaining two minutes always being sufficient for this purpose. At the end of the ten minutes the high speed clutch was again thrown in, the stop-watch started anew, and the bath cooled another five degrees. where it was again held until another ten minutes had elapsed, tally being taken as before ; this operation was repeated until such time as all tubes had been brought to solidify ; this being done, another heating and cooling could be carried out at any time. The results were recorded on specially prepared tally sheets, on which were one hundred vertical columns, divided into groups of twenty-five ; thus each tube had its own individual column ; two such tally sheets were prepared, one for each thermostat. The tally sheets were also divided into horizontal columns, in groups of five. each horizontal column corresponding to a given temperature of supercooling. For convenience in reading off the tubes, each bunch of twenty-five tubes, contained in one holder, was numbered, and also subdivided into groups of five by means of small rubber bands stretched over them. With the aid of these devices it was a fairly easy matter for one operator to read off the tubes while the other kept the tally.

From the very start considerable difficulty was encountered on account of the occasional breaking of tubes ; this was particularly noticeable among the evacuated tubes. Only rarely was it possible to heat a set of one hundred tubes without the breaking of at least one of them, while frequently two or three would break. On account of this, the stock of extra tubes was kept continually in the thermostats, in order that they might receive the same treatment as those in the holders, and thereby furnish a satisfactory supply for the replacement of broken tubes.

In stocking the thermostats at the outset. fifty evacuated and fifty unevacuated tubes were placed in each : as the reserve supply of evacuated tubes soon gave out, it became necessary to supply them with unevacuated ones. It soon became evident that evacuation had no marked influence on the conduct of the tubes. and no further reference need be made to them.

By the above method a large number of results were obtained. Since the printing of the complete tally sheets would demand a large amount of space, the results are summarized. and only the total percentages given : these will be found in the accompanying table. (Table I.) In this table the results under A are for one thermostat, those under B for the other. The results are arranged in the order in which they were obtained, and each heating and cooling. constituting a complete experiment, is numbered at the left, so that by reading through the tables as they are given,

one can follow the whole history of the tubes contained in either thermo-stat, except that replaced tubes cannot be indicated. In all cases θ indi-cates the time of heating, in hours ; T the temperature of heating ; and small δ, where used, indicates the time which the tubes had stood between heatings, with their contents in the solid state. The temperatures of the coolings. which were the same in all cases, are given at the tops of the last ten columns. The figures indicate the *total* percentages of tubes which had solidified, and not merely those which had solidified during each ten minute period.

It was early noticed that when solidification started, it was always a metastable form of the *p*-nitrotoluene which appeared. This form was much more translucent than the ordinary one, grew very slowly, and after persisting for a short time, went over into the very rapid-growing ordinary form. In the experiments, it was of course the supercooling with respect to this metastable form which was always observed, as this form invaria-bly appeared first.

In interpreting these results, we have assumed that it is largely a matter of chance whether a tube does or does not solidify when subjected to a given degree of supercooling for a given time. The factor of probability increases rapidly with the degree of supercooling, being, in the case of *p*-nitrotoluene, very small at 46°.2, and practically infinite at 26°.2, except after high and long continued heatings. This factor of probability is very much influenced by the treatment to which the substance has been previously subjected, as the results of this investigation show. In this case, as in others where the factor of probability enters, very considerable discrepancies are to be expected in individual experiments, just as in the throwing of the dice. Too much importance must not therefore be attached to occasional conflicting results, but the conclusions rather be drawn from a broad consideration of the results as a whole. It was in order to reduce such chance fluctuations to a minimum that so large a number of tubes were subjected to investigation.

This investigation was carried out for the purpose of answering the following questions :

1. Do the individual tubes show anything which could be construed as habit ? That is, is there any tendency for a given tube to consist-ently supercool to a greater or less extent than its neighbor ?
2. What is the influence of the time of heating ?
3. What is the influence of the temperature of heating ?
4. To what extent are the above effects permanent and to what extent reversible ?

These questions will now be discussed in the order here given.

1. *Habit.* A study of the complete tally sheets is of course necessary to determine whether or not any individual tubes show habit. Since these

TABLE I.

No.	T. A	T. B	θ A	θ B	δ A	δ B	46.2° A	46.2° B	41.2° A	41.2° B	36.2° A	36.2° B	31.2° A	31.2° B	26°.2 A	26°.2 B
1	81.2	61.2	3.5	0.5	....	....	0	1	3	22	49	89	96	100	100	100
2	81.2	81.2	0.5	3.5	....	....[1]	5	...	13	...	63	...	95	...	100	...
3	81.2	61.2	3.5	0.5	....	1.0	0	...	3	...	...	...	...	...	...	...
4	81.2	81.2	0.5	3.0	0.5	....	...	...	6	...	39	...	87	91	100	100
5	81.2	61.2	3.0	0.5	....	1.0	0	0	...	8	...	53	...	...	100	100
6	81.2	81.2	0.5	8.0	0.5	....	2	...	10	...	33	...	88	...	100	...
7	81.2	61.2	8.0	0.5	....	24.0	...	2	...	10	...	42	...	86	...	...
8	81.2	81.2	0.5	5.0	24.0	24.0	1	0	7	1	26	12	83	55	100	100
9	81.2	61.2	5.0	0.5	24.0	21.0	0	0	0	5	4	30	55	72	99	100
10	81.2	61.2	0.5	0.5	24.0	72.0	1	0	9	6	25	26	84	73	100	100
11	81.2	61.2	0.5	0.5	72.0	1.0	1	0	5	2	23	26	68	84	100	100
12	61.2	61.2	0.5	5.0	1.0	24.0	1	0	2	1	26	14	84	63	100	100
13	61.2	61.2	5.0	0.5	24.0	24.0	0	0	4	4	6	14	64	70	100	100
14	61.2	61.2	0.5	5.0	24.0	24.0	0	0	1	1	6	6	71	65	99	100
15	61.2	61.2	5.0	0.5	24.0	24.0	0	0	0	4	6	15	63	73	99	100
16	61.2	61.2	0.5	0.5	24.0	240.0	1	0	5	2	15	8	69	52	100	100
17	61.2	61.2	0.5	24.0	240.0	1.0	0	0	1	0	12	4	59	33	100	100
18	61.2	61.2[2]	24.0	48.0	1.0	1.0	0	2	0	2	5	6	46	34	98	97
19	61.2	61.2	72.0	0.5	1.0	72.0	0	0	1	2	5	12	38	54	98	100
20	61.2	61.2	0.5	92.0	72.0	1.0	0	0	1	1	10	7	52	31	99	92
21	61.2	61.2	92.0	0.5	1.0	1.0	0	0	1	2	4	12	40	65	93	100

[1] In some cases, for certain reasons, tubes were given definite heating and cooled without readings being taken. In such cases values for T. and θ are given.

[2] In these heatings, the regulator failed to shut off the heat, and the temperature rose during the night to between 80° and 90°.

No.	T. A	T. B	θ A	θ B	δ A	δ B	46.2° A	46.2° B	41.2° A	41.2° B	36.2° A	36.2° B	31.2° A	31.2° B	26.2° A	26.2° B
22	61.2	61.2	0.5	0.5	1.0	72.0	0	1	0	1	9	9	68	60	98	100
23	61.2	61.2	0.5	0.5	96.0	0.1	1	1	3	2	16	21	54	66	100	100
24	61.2	61.2	0.5	0.5	0.1	0.1	1	1	5	2	23	16	69	68	100	100
25	61.2	61.2	0.5	0.5	0.1	0.1	1	1	3	3	23	20	73	72	100	100
26	61.2	61.2	0.5	0.5	0.1	48.0	0	0	0	2	16	15	73	47	99	100
27	61.2	61.2	0.5	0.5	24.0	120.0	0	0	4	2	19	13	60	52	100	100
28	61.2	61.2	0.5	0.5	0.1	0.1	0	0	1	1	23	15	71	64	99	100
29	61.2	61.2	0.5	0.5	120.0	....	1	..	2	..	15	..	57	..	100	...
30	61.2	61.2	0.5	0.5	0.1	0.1	0	0	3	1	20	16	62	64	100	100
31	61.2	61.2	0.5	0.5	....	144.0	..	1	..	3	..	8	..	47	..	100
32	61.2	61.2	0.5	0.5	0.1	4.0 [1]	0	1	3	3	18	13	70	74	100	100
33	61.2	61.2	0.5	4.0	168.0	....	0	0	2	0	7	2	40	26	100	98
34	61.2	52.0	0.5	1.0	0.1	0.1	0	0	2	5	17	23	62	88	96	100
35	61.2	51.7	4.0	47.0	....	72.0	0	0	0	0	3	3	28	51	82	97
36	52.0	61.2	2.5	0.5	0.1	288.0	0	0	2	1	18	4	76	36	99	99
37	51.7	61.2	46.0	0.5	72.0	1.0	0	0	1	3	8	11	45	47	91	98
38	61.2	61.2	0.5	27.0	288.0	20.0	0	0	2	0	13	4	43	30	97	96
39	61.2	61.2	26.0	0.5	20.0	0.1	0	0	0	0	2	6	26	49	93	99
40	81.2	81.2	0.5	0.5	48.0	48.0	0	0	0	0	3	0	23	22	97	95
41	61.2	61.2	0.5	0.5	0.1	0.1	2	0	6	2	16	9	70	55	99	99
42	81.2	81.2	0.5	0.5	....	....	0	0	0	0	0	0	9	16	71	72

[1] The tubes in this case had been held for four hours at 0° C., which probably accounts for the unusually high results.

NOTE.—In Experiments 33, Thermostat B., 35, Thermostat A., and 42, Thermostats A. and B., heatings were carried out subsequent to the heatings given in the table, but without any intermediate cooling or solidification. In Exp, 33, the Temp. of the heating was 51.7, the time 46; in Exp. 35, the Temp. was 51.7, the time 44; in Exp, 42, the Temp. in both thermostats was 51.7 and the time 24.

sheets are not given here, the discussion of this question will have to be confined to statements of conclusions which have been reached as a result of the study of those sheets.

That some, at least, of the tubes do show a very noticeable habit, is beyond doubt. For example, one tube contained in thermostat A. very rarely solidified until the temperature of 26°.2 was reached, and frequently, after the first few heatings, did not come down at that temperature in the allotted time; it would always come down at this temperature if more time was given; similar conduct on the part of other tubes was frequently noted. Other tubes were found which would consistently solidify at the higher temperatures; curiously enough, this habit may be modified to a considerable extent, as will be pointed out later. The great majority of tubes showed no marked habit : *i.e.*, tubes which solidified early in one experiment might solidify late in another, and *vice versa*.

2. *Time of Heating.* At the very outset it became evident that the heating of the tubes produced a very considerable permanent effect, in such a way that the tendency to supercooling was markedly increased. After several heatings, this permanent effect, although it had not reached its full value, became so nearly constant that fairly definite conclusions as to temporary effects could be drawn. The effect of the time of heating can be very readily seen by reference to Experiments 17 to 22 in both thermostats; all these experiments were carried out with 61°.2 as the temperature of heating, and so made that short and long heatings alternate. The increased tendency to supercool after long heatings is seen to be very marked in all cases; very nearly the maximum effect seems to have been reached after 24 hours. Numerous other instances of the effect of the time of heating may be found throughout the tables.

3. *Temperature of Heating.* Avoiding again the first few heatings, on account of the magnitude of the permanent effect, the influence of the temperature of heating is seen by comparing Experiments 39 and 40 in thermostat B., 38 and 40 in thermostat A., as well as 34 and 36 in both thermostats, where even with shorter time of heating at the higher temperature, the effect of the higher temperature is to produce a greater tendency to supercooling. Many other instances may be found; thus a higher temperature of heating invariably reduces the number of tubes solidifying under given conditions of cooling, or, as it has been expressed in a previous paper, increases the degree of sterilization. The intention had been to carry out a series of heatings to temperatures as high as 100°, but on account of the great mortality among the tubes at higher temperatures, this was put off until the last. The damage caused by the recent earthquake, however, made these, as well as some other projected experiments, impossible.

4. *Permanency of the Effects.* The question as to what extent the above effects are permanent or reversible. It has already been stated that a sort of permanent sterilization was producible by heating the tubes; in fact, the first ten heatings were carried out with the purpose of forcing this permanent sterilization to its maximum. The plan was to heat for five hours at a relatively high temperature (81°.2), bring the tubes to solidification without taking any readings, then to heat for one-half hour at 61°.2 and to cool with readings. The heating at 81°.2 was then repeated, followed again by the heating at 61°.2, when the reading would show if any permanent effect had been produced. (See Exps. 1–10.) The permanent effect of the first few heatings is very apparent. From Experiment 10 onward, it was assumed that the permanent effect produced would be so small that it would probably not mask other effects. This proved to be the case, although some permanent effect was still produced, as may be seen by comparison with some of the later heatings to 61°.2 for half an hour.

That the whole effect of the heating is not permanent is very readily seen from the fact that tubes which had been heated to high temperatures, solidified, and then heated to low temperatures only, recover to a great extent from their sterilizing. Abundant instances will be found by reference to the table.

If the sterilization is due to some slow reaction taking place in the heated liquid, it may or may not be reversible; the question as to this reversibility may be readily subjected to experimental proof. For this purpose the tubes were heated to a high temperature for a definite time and then cooled to just above the melting point and held there for one or two days, in order that the reverse reaction, if it occurred, should have ample time to complete itself, or at least to make itself felt. Under these conditions, if the reaction is reversible, the tubes should show the properties of low heated tubes on solidification; if irreversible, they should show the prop·erties of high heated tubes. No evidences of reversibility were obtained in any case. Thus in thermostat B., Experiment 33, the heating was carried on for four hours at 61°.2, the temperature then dropped for forty-six hours to 51°.7, and finally the usual cooling carried out. In Experiment 35, the heating at 51°.7 for the same length of time was carried out without the previous heating at 61°.2. A comparison of the two cases shows no tendency toward a reversion from the effects of the high heating. The same thing is shown in Experiments 35 and 37 and Experiments 40 and 42 in thermostat A.; also in Experiments 40 and 42 in thermostat B.

A careful study of the tabulated results given above shows beyond doubt that the factors which have been discussed are of great influence in determining the conduct of the supercooled fusions of *p*-nitrotoluene. On

the other hand, discrepancies exist in the numerical data obtained, which are so great that they can only be explained on the assumption that other factors play a part in controlling the degree of supercooling to which such fusions are susceptible. While the experiments were being carried out, it was noticed that if the tubes had been allowed to stand for two or three days with their contents in a solid state, abnormally low results were obtained when they were subjected to a subsequent heating and cooling. It was also noticed that when the tubes were reheated for a second time, very soon after they had been forced to solidify, unusually high results were obtained. Furthermore, in the latter case, tubes which had been in the habit of coming down late were very likely to change this habit, and to come down early, and *vice versa*. Here, of course, tubes which came down late would have remained in the solid state for considerably less time before reheating than would those which came down early. All of these observations seemed to indicate that the length of time which the substance had been solid was of influence in determining the conduct as to supercooling.

A series of experiments was run for the express purpose of determining whether or not this suspected influence was active. After standing for several days in the solid state, the tubes were heated for half an hour to $61°.2$; they were then cooled as usual and the tally taken. They were then immediately reheated again for half an hour to $61°.2$, and again cooled and tally taken. The results were much higher in the second case than in the first. The immediate reheating was then twice repeated, and closely agreeing results obtained. The data for these experiments are to be found under Experiments 23 to 26 in thermostat A. and Experiments 22 to 25 in thermostat B. Following these immediate reheatings, the tubes were again allowed to stand in the solid state for a considerable length of time, after which low results were again obtained. Subsequent immediate reheatings again raised the results. (See table.)

The tally sheets had been dated from the outset, so that it was possible in all cases to determine, at least approximately, the time during which the tubes had remained in the solid state between heatings. A careful examination of the whole table, taking into account the values of δ as given, will serve to confirm the above conclusions as to the influence in question.

SUMMARY OF RESULTS.

In so far as conclusions may be drawn from these studies with *p*-nitro-toluene, the following may be considered as a summary of the most important influences which are active in determining the degree of super-cooling to which a fused substance may be subjected :

(1) Certain tubes containing the substance show an habitual tendency to supercool to a much greater extent than the average, while

others habitually supercool less than the average. In general, the great majority of tubes show what may be termed normal conduct, solidifying now high and now low. We have no rational explanation for the existence of these habitual peculiarities. Possibly they are due to unevenly distributed dust particles. or to peculiarities in the walls of the tubes.

(2) The time for which a tube has been heated to temperatures above its melting point is of great influence upon the readiness with which it will afterward solidify, in such a way that the longer the time of heating the greater the difficulty of bringing the tube to solidify. Thus there is a sort of sterilization which increases with the time of heating.

(3) The higher the temperature to which the tube is heated, the greater is the degree of sterilization.

(4) To a certain extent the sterilization produced by heating is permanent ; thus tubes that have been heated for a long time at rather high temperatures do not return to their original condition, but remain more sterile than those which have not been so treated. This may be due to some slight chemical reaction, which is furthered by the heating, or to a gradual attaining of some sort of equilibrium between the substance and the walls of the tube, or perhaps between the substance and the dust particles. If due to chemical action, this action can scarcely be oxidation by the air contained in the tube, because evacuated tubes showed practically the same conduct as unevacuated. After repeated heatings, the permanent effect seems to approach a maximum.

(5) To a great extent the sterilization is not permanent, but is merely a condition that is nullified by a subsequent solidification.

(6) The reaction which produces the sterilization is not reversible in the liquid state, since the maintaining of the substance in the liquid state, at temperatures just above the melting point, after previous treatment at higher temperatures, results only in increased sterilization.

(7) The effect of allowing the substance to remain for various lengths of time in the solid state is both peculiar and unexpected. The action is such that a long time in the solid state tends to produce a greater sterilization upon subsequent heating than would occur if the time in the solid state had been short.

(8) The influence of the time and temperature of heating allow of explanation in terms of the nuclear hypothesis (see previous papers), while the influence of the time in the solid state is difficult to explain by this hypothesis.