889. *A Study of the Supercooling of Drops of Some Molecular Liquids.*

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The extent to which various liquid drops may be supercooled has been observed by examining the appearance of clouds of such drops in a beam of light at different temperatures. For most of the liquids studied the great majority of the drops did not freeze until a comparatively narrow range of temperature had been reached far below the melting point. In this range where the drops freeze spontaneous homogeneous nucleation is assumed to occur. This is discussed in the light of current theories of nucleation phenomena in which a key role is played by the interfacial tension between solid and liquid. An attempt is made to determine values of this quantity, and correlate them with the corresponding heats of fusion.

IN recent years measurements have been made, particularly by Turnbull and his colleagues, on the extent to which liquid metals will supercool in the absence of catalysts (Turnbull and Cech, *J. Appl. Physics*, 1950, **21**, 804). An essential feature of these experiments was that observations were made on numerous, isolated drops, in the expectation that while some of these might have occluded impurities the majority should not. Experiments on the same lines with molecular liquids with the single exception of water have not been described. In this paper we present some observations on the supercooling of some common organic liquids and of some liquefied gases. An attempt will be made to interpret these on current theories of homogeneous nucleation.

EXPERIMENTAL

The problem was to find the temperature at which a large number of isolated drops of liquid froze. One may in principle either examine a cloud of drops simultaneously or else a large number of individual drops. An unsuccessful attempt was made to follow the latter course, by adapting Rumpf and Seigl's method (*Z. Physik*, 1938, **111**, 301), in which individual drops were held stationary and observed in a cold stream of air flowing upwards. It was found that it was not easy to hold a drop stationary, that the drops steadily evaporated, and that freezing could not readily be detected. Consequently, a cloud method was adopted. The method had been used for water, though few experimental details were given (Schaefer, *Bull. Amer. Met. Soc.*, 1948, **29**, 175), and it was reported that the water clouds froze completely over the range $-39° \pm 0{\cdot}1°$.

A copper vessel was made with shape and dimensions shown in Fig. 1, *A*. The inside was blackened by electrolytic deposition from a solution containing nickel, to provide a black background to contrast with the twinkling of crystals. A brass lid (Fig. 1, *B*) was screwed on to the lip of this chamber; it had four tubes (Fig. 1, *C*) soldered on to it, one reaching nearly to the bottom of the chamber, this one being used as an exit for dry air; down another came wires for the two thermocouples which ended near the middle and near the bottom of the vessel, and which were held on a mica former attached to the lid; a third held the glass tube for introducing the vapour to make the clouds, and down the fourth solid carbon dioxide could be dropped. The lid also had a circular hole 5 cm. in diameter on to which was clamped a piece of Perspex. A beam of light was reflected off a mirror so that it entered the chamber through the Perspex at an angle of 45°. The cloud in the chamber was observed through a vertical glass tube 1·5 cm. in diameter blackened on the outside, which fitted over a hole in the Perspex window. The upper end of the tube was covered with another piece of Perspex and the tube was sufficiently long to ensure that this did not frost over.

FIG. 1.

First cloud chamber used to examine freezing of drops.

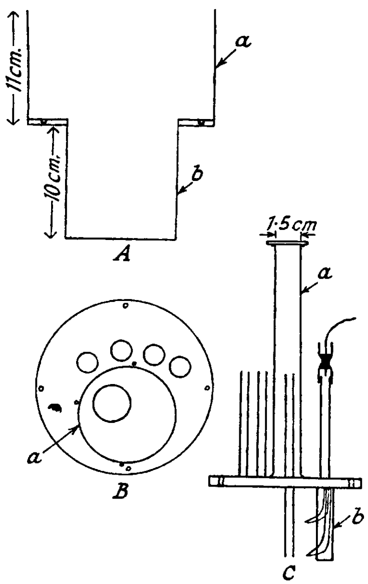
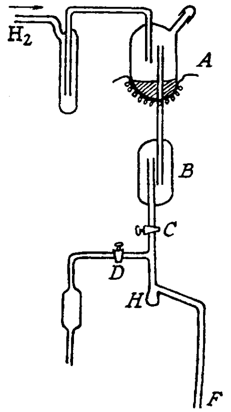


FIG. 2.

Apparatus used for introducing vapour into cold chamber.



Key to Fig. 1:

A. Copper chamber in elevation:
  (*a*) Thin copper shield;
  (*b*) copper 1·5 mm. thick.
B. Brass lid of chamber in plan:
  (*a*) Perspex window with hole for viewing tube.
C. Lid in elevation:
  (*a*) Viewing tube blackened on outside;
  (*b*) thermocouples on mica former.

The chamber and lid were immersed to within 1 cm. of the top edge of the copper shield in a bath of alcohol contained in a Dewar vessel. The alcohol was cooled with solid carbon dioxide, and was stirred and kept cold by a stream of cold gas evolved from liquid oxygen, the rate of this stream being controlled by adjusting the current in a heating coil immersed in the liquid oxygen. The temperature of the bath, measured to within ±0·1° by a three-junction thermocouple, could be kept constant without difficulty for the time required to make and observe a cloud.

The temperature of the clouds, which often only lasted a short time, was measured with the thin bare thermocouples mentioned above. The second junction of these thermocouples was immersed in the surrounding bath. By connecting the thermocouples to a galvanometer, the difference in temperature between the thermocouple junctions in the chamber and in the bath could be seen at any instant. A deflection of 3 cm. on the galvanometer scale corresponded to a temperature difference of 1°.

The best method of producing a sufficiently copious cloud while at the same time avoiding excessive heating, was found to consist of blowing a puff of vapour into the cold chamber usually together with some indifferent gas. The apparatus used is shown in Fig. 2. By means of a heating coil, liquid was boiled in the bottom of *A*; *B* and *H* served as traps for any large quantities of liquid that might be blown down, and *B* could be surrounded with ice or hot water. *F* reached into the chamber; usually it was used with a hole in the side of the tube, and the bottom sealed, in order that the vapour should be blown around the chamber, but it was subsequently found that it was usually better simply to have the bottom open.

The liquid was boiled in *A*, which was filled with hydrogen (chosen for its high thermal conductivity) which had been passed through a liquid-oxygen trap, to a pressure of a few cm. of mercury. The tap *C* was then opened, and a cloud would appear in the chamber. This was illuminated by the beam of light and observed through the blackened tube; if the cloud sparkled it consisted of crystals, if it appeared as a dull mist it consisted of unfrozen drops—though by no means every liquid gave such clear-cut results. A further test of an unfrozen cloud was to drop in small particles of solid carbon dioxide, which, providing the freezing range for the substance in question lay above $-78°$, would produce in their wake " trails " of tiny crystals which grew by distillation until the whole cloud was transformed into a mass of large sparkling crystals. Solid carbon dioxide had of course no effect on a frozen cloud.

If a substance was examined which was solid above room temperature, all of the boiler and the inlet tube down to the chamber was electrically heated; often with these substances it was not necessary to boil the liquids, which were simply kept molten. After each cloud, *C* was closed and *D* opened, and a stream of dry air passed through the chamber, which removed the solid residue from the previous cloud. Finally, *D* was closed and when temperature equilibrium had been regained another cloud was formed. The temperature was altered by warming or cooling the surrounding bath.

When each cloud was formed the temperature in the chamber rose; usually the thermocouple indicated a maximum difference of temperature between the bath and the chamber of 1—2°. As soon as the thermocouple E.M.F. has passed its maximum value the gas temperature must be less than that of the thermocouple junction; the clouds nearly always persisted until the maximum value had been reached and usually until their temperature was within a fraction of a degree of that of the bath. The recorded temperatures are those of the bath, so these represent the lowest cloud temperatures at least to within a degree and usually to within a fraction of a degree.

Frequently, two samples of a single substance were examined which differed in purity. However, there was hardly any difference in the behaviour of such a pair of samples, and we have no evidence for believing that the results we present are in any way critically dependent on the concentration of homogeneous impurities. The only exception to this statement concerns the presence of water (see, *e.g.*, remarks on benzene, below); but the effect here is almost certainly due to the formation of ice particles which act as heterogeneous nuclei. Accordingly, all liquids and gases were dried with phosphoric anhydride except for dioxan and ammonia, for which sodium was used, and precautions were taken to exclude moisture and in particular carrier gases were carefully dried.

The observations on different substances may be summarised as follows. (For convenience we shall denote by T_c the mean temperature of the comparatively narrow range in which the drops were first observed to freeze.)

Water.—Distilled water was used, and was found to freeze over the range $-40{\cdot}5° \pm 1°$. Above the critical temperature, $-40{\cdot}5°$, but below 0°, a cloud could be frozen by dropping in solid carbon dioxide. Several degrees above T_c a few crystals appeared, but the main part of the cloud remained unfrozen; this was generally so for all the substances examined. Below T_c the clouds always froze and solid carbon dioxide had no effect. When the drops freeze spontaneously the crystals are rather smaller than those produced by carbon dioxide in an unfrozen cloud; probably the latter grow by distillation.

Other workers, sometimes using different techniques, have reported similar temperatures to that recorded here for the spontaneous freezing of small water drops. Schaefer (*loc. cit.*) gave $-39° \pm 0{\cdot}1°$ (though it is surprising that such a narrow range is reported); Mason (*Quart. J. Roy. Met. Soc.*, 1952, **78**, 22) gave $-40° \pm 1°$, and Lafargue (*Compt. rend.*, 1950, **230**, 2022) quoted $-40{\cdot}5° \pm 1{\cdot}5°$.

Benzene.—Two samples of benzene were examined; the first and less pure had m. p. 5·17°; the second, m. p. 5·50°, was purified by the method involving the formation of a clathrate compound (Evans, Ormrod, Goalby, and Staveley, *J.*, 1950, 3346). The first sample seemed to freeze a degree or so above the second sample, which froze over the range $-65° \pm 2°$. Solid carbon dioxide caused unfrozen clouds to freeze. If the benzene was damp, freezing occurred above *T*., but not above about $-45°$; possibly ice formed in each drop catalysed the freezing of the benzene.

Carbon Tetrachloride.—Two samples were used. The first was the purest commercial sample available; the second was the same liquid further purified by washing it twice with sodium hydroxide solution, three times with water, drying ($CaCl_2$), and finally fractionating off phosphoric anhydride. The fraction collected boiled over a range of 0·05°. Again, there was an indication that the less pure sample froze a degree or so above the purer sample, which froze at $-73° \pm 2°$. Solid carbon dioxide caused freezing of unfrozen clouds.

Ethylene Dibromide.—A sample melting at 8·3—9·5° froze about 2° above a sample which had been purified by succesive treatment with sulphuric acid, sodium carbonate, and water and then fractionated; this purer sample, m. p. 9·3—9·8°, froze at $-57° \pm 2°$. With this substance it was not easy to distinguish between frozen and unfrozen clouds; the frozen particles did not sparkle brightly, but lasted longer and were brighter than the liquid drops. Probably this was because smaller drops were formed in this case than before. Solid carbon dioxide, especially if present in the chamber when the cloud was being made, caused large crystals to appear.

Naphthalene.—A sample of high purity was available, which had been obtained by slowly freezing naphthalene and rejecting that portion which froze last (Schwab and Wichers, *J. Res. Nat. Bur. Stand.*, 1940, **25**, 747). It gave clouds that froze over the range $-14·5° \pm 1°$. Solid carbon dioxide had the usual spectacular effect of forming large crystals in an unfrozen cloud.

Benzoic Acid.—" AnalaR " benzoic acid was used. Very dense and long-lasting clouds were produced which did not sparkle at any temperature unless solid carbon dioxide was added. Then, providing the temperature was above about 4°, the carbon dioxide caused after a short time the appearance of many sparkling crystals. But at 0° carbon dioxide had no effect. Hence, one may conclude that the drops froze between 0° and 4°, though they were too small to sparkle visibly when they all froze together; when, however, a few were frozen by local cooling, these could grow by distillation to larger crystals. This evidence is not as direct and therefore not as reliable as that obtained for some other substances, but the conclusion is thought to be essentially correct.

Carbon Tetrabromide.—Two samples were examined, the purer being obtained from the other sample by sublimation at low pressure. The experiments with this substance were not easy, chiefly because the clouds remained in view for only a very short time. They often disappeared before the thermocouple had reached its maximum value. This is probably connected with the high density of the tetrabromide. Also, to produce copious clouds the substance had to be boiled and this caused some decomposition and a large heating effect when the cloud was made. The particles were, however, quite large, so it was easy to tell whether or not they were frozen. The first sample seemed to freeze near +18°, and the second at $+8° \pm 5°$. The reason for this difference, upon which too much reliance should not be placed, may be connected with the difference in purity; 8° will be used for T_c in later calculations. Solid carbon dioxide caused freezing as usual.

Diphenyl.—Again two samples were examined: the first a commercial sample, the second purified by two low-pressure sublimations. The clouds consisted of very small particles and lasted as long as 10 minutes. An unfrozen cloud was detected by adding solid carbon dioxide after 1 minute, whereupon general freezing would occur. A cloud at a temperature above what was taken to be T_c would often develop crystals spontaneously after about 5 minutes; it was considered that this was due to the long period of time for which the cloud was in contact with solid on the walls. Again, therefore, the results are not as clear-cut as those yielded by more favourable substances. The direct sample seemed to freeze over the range $-15° \pm 1·5°$. The purer sample at first probably gave liquid clouds 5—8° below this figure, but later T_c returned to $-15°$.

For the eight substances just mentioned it was possible to define with varying degrees of precision the freezing range. For the following liquids this could not be done.

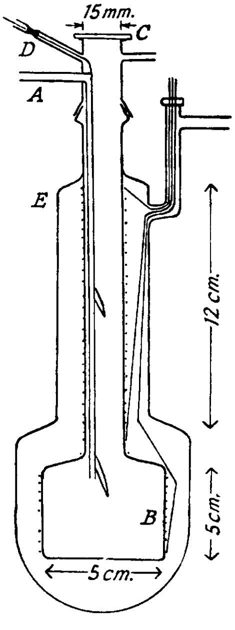
cyclo*Hexane.*—Two specimens were examined, one melting at 3·8°, the other at 4·98°. These specimens were not therefore of the highest purity, but the lack of success with them did not seem to justify the preparation of a purer sample. Consistent results could not be obtained; freezing may have taken place anywhere between $-40°$ and $-60°$. Sometimes at a particular temperature a cloud appeared to be frozen and sometimes unfrozen. Assuming that freezing should occur over a small temperature range, one is led to suppose that there is some extraneous interfering factor. It is hard to see how such a factor could do other than raise the freezing temperature; crystals on the walls of the vessel might cause early freezing and so might impurities, for if these were homogeneous impurities which raised the interfacial tension between solid and liquid, they would for this very reason be largely eliminated from the interface. Thus T_c probably lies at or below $-60°$.

Dioxan.—A purified sample was used which melted at 11—11·7°. Freezing probably took place between $-44°$ and $-54°$, but the results were not very consistent.

p-*Xylene.*—In all, three samples were examined, m. p.s 12·6°, 13·1—13·3°, and 13.2—13·3°. No difference could be detected in their behaviour. Down to about $-50°$ solid carbon dioxide caused the clouds to freeze and this could be detected by the twinkling of the crystals. Below this, the effects were much less definite, possibly because the drop size decreased, and no definite freezing range was found.

FIG. 3.

Second apparatus used for examining clouds at low temperatures.

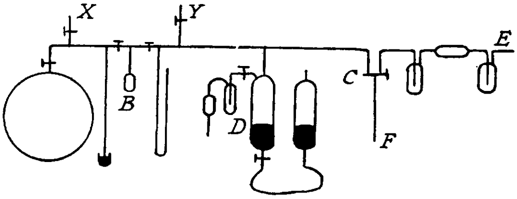


Apparatus used at Low Temperatures.—In order to extend the temperature range below $-78·5°$, a new all-glass cloud chamber was constructed (Fig. 3) which could be immersed in liquid oxygen. The temperature inside the chamber could be controlled by the current in the surrounding heating wire and by the pressure of gas in the space between the inner and the outer walls. The temperature was measured with two 36 s.w.g. copper–38 s.w.g. constantan thermocouples which had been calibrated at the temperatures of solid carbon dioxide and boiling oxygen; one terminated half way down the narrow lead-in tube, and the other in the centre of the main chamber.

Substances gaseous at room temperature were examined and were introduced into the chamber by means of the apparatus shown in Fig. 4. The chamber was surrounded by a Dewar vessel with an unsilvered strip which contained liquid oxygen up to the level *E* (Fig. 3). After the chamber had been filled with dry hydrogen, its temperature was brought to some value below the m. p. of the substance being examined, and the temperature of the lead-in tube was kept, by adjusting the heating current, just above the m. p. Some gas from the trap *B* was compressed in the vessel *D* (which was of about the same capacity, *viz.*, 100 c.c., as that of the cloud chamber), to a pressure of about 20 cm. of mercury above atmospheric. With the chamber in contact with the atmosphere through a liquid-air trap, tap *C* was opened and a cloud formed in the chamber. It was illuminated by a beam of light directed slightly upwards shining through the Dewar vessel, and it was examined from the top through the plate-glass window *C*. The outside of the bottom of the chamber was blackened with "Aquadag." As usual, crystals generally sparkled in the light beam, while liquid drops appeared as a dull fog. When a cloud was formed the temperature rose at first and then fell, but it usually became constant about 1° above the initial temperature so that the recorded temperatures are perhaps low by this amount, though it did seem that whatever happened to a cloud happened in the first instant in which it was made. After each cloud, solid in the chamber was removed with a stream of air from *E* which was dried with phosphoric anhydride and passed through a liquid-oxygen trap, and the temperature was readjusted and the operations repeated.

FIG. 4.

Apparatus used for introducing gases into the low-temperature cloud chamber which is connected to the tube F. *The vacuum line is connected to* X *and* Y.



The following results were obtained.

Ammonia.—The ammonia, prepared from magnesium nitride and water, had been dried with sodium and purified by fractional sublimations; its triple point pressure was $45·62 \pm 0·03$ mm. Freezing took place at $-118·0° \pm 1·5°$; a few crystals were seen above this temperature, but mostly there was a dense fog which disappeared within about 30 seconds. At and below T_c the twinkling of the crystals was easily observable.

Methyl Chloride.—Two samples were examined; both were obtained from a cylinder and dried by passage through calcium chloride and phosphoric anhydride. One sample was further purified by distillation in a low-temperature column (Clusius and Riccoboni, *Z. physikal. Chem.*, 1938, *B*, **38**, 81). Again no difference was observed between the two specimens.

The unfrozen clouds appeared as bright thick fogs, but below about −154° remarkable white lumps or fibrous filaments appeared which did not sparkle, and settled only slowly. Though their like had not been seen before, these particles were assumed to be frozen. It may be significant that often rather feather-like crystals were seen in the liquid-oxygen trap containing the methyl chloride. It was estimated that freezing took place over the range −153·2° ± 1·5°.

Hydrogen Sulphide.—This was prepared by dropping 2N-hydrochloric acid on calcium sulphide, washing the gas with water and potassium hydrogen sulphide solution, and drying it with calcium chloride and phosphoric anhydride. A portion was examined at this stage and the rest was purified in the low-temperature column. Undoubtedly, the second sample was purer than the first but no difference between the two could be detected. Above about −100° clouds could not be formed; between about −100° and −115° frozen clouds could be obtained with fairly large crystals which quickly settled. Below about —115° the clouds lasted longer, but sparkling could not definitely be seen presumably because the particles were small, though it is assumed that crystals were present. It seems therefore that in these experiments liquid hydrogen sulphide supercools less than about 15° before it freezes.

Nitrous Oxide.—Nitrous oxide was obtained from a cylinder, passed over phosphoric anhydride and fractionated in the low-temperature column. Because of the high vapour pressure (the triple point pressure is 658·9 mm.) clouds could not be produced above about −127°, and even here very large puffs were required to give no more than a few wisps of crystals and there was a heating effect of as much as 4°. Between about −127° and −131° frozen clouds were obtained which were thin and lasted only about 10 seconds. A few degrees below this, better clouds were obtained but it was now not easy to tell whether or not crystals were present, though presumably this was the case. It seems therefore that there was less than about 25—30° of supercooling.

Hydrogen Chloride.—Hydrogen chloride was prepared from benzoyl chloride and water, passed through a trap at the temperature of solid carbon dioxide, and then distilled in the low-temperature column. No satisfactory results could be obtained with this substance. Clouds could be produced within about 10° of the m. p. and sometimes there were suggestions that these contained crystals. At lower temperatures brighter and longer-lasting clouds were produced but it was not possible to decide definitely whether or not they were frozen.

DISCUSSION

We shall first consider the results obtained in the light of the expression derived by Turnbull and Fisher (*J. Chem. Phys.*, 1949, **17**, 71), by application of absolute reaction rate theory, for the rate of nucleation in supercooled liquids, *viz.*:

$$r^* \approx (nkT/h) \,.\, \exp(-\Delta F_A/kT) \,.\, \exp(-\Delta F_i^*/kT) \quad . \quad . \quad . \quad . \quad (1)$$

where r^* is the number of self-propagating nuclei formed per second in a drop of liquid containing n molecules, and ΔF_A was defined by Turnbull and Fisher as the free energy of activation for the short-range diffusion of atoms or molecules moving a fraction of an atomic distance across an interface to join the lattice of the nucleus; ΔF_i^* is the free energy of formation of a nucleus of critical size; its value at a temperature T is given by the following expression

$$\Delta F_i^* = 16\pi\sigma^3 T_0^2/3\lambda^2(\Delta T)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where σ is the solid–liquid interfacial-surface free energy per unit area, λ is the latent heat of fusion per unit volume, T_0 is the m. p., and $\Delta T = T_0 - T$. This expression is derived by assuming that the nuclei are spherical, and that the entropy of fusion is independent of temperature.

Turnbull has applied these equations to his own observations on the freezing of supercooled liquid metals (Turnbull, *J. Appl. Physics*, 1950, **21**, 1022; *J. Chem. Phys.*, 1952, **20**, 411). For two of these (*ibid.*, 1950, **18**, 768), measurements were actually made of the nucleation rate at different temperatures. These measurements were in fair quantitative agreement with equation (1) if ΔF_A was taken to be the (relatively small) free energy of activation for viscous flow. For each of a large number of metals, measurements were made of the temperature in the near neighbourhood of which the nucleation rate rises to such a figure as to cause nucleation in, and hence crystallisation of, a small drop (diameter $\sim 50\ \mu$) in ~ 10 seconds. From equations (1) and (2), values of σ for these metals were derived. There is apparently no other method for estimating σ. Turnbull's values are such that the quantity $\sigma_g/\Delta H_f$ for most metals lay between 0·4 and 0·5. Here ΔH_f is the molar heat of fusion and $\sigma_g = N^{\frac{1}{3}}V^{\frac{2}{3}}\sigma$, where N is the Avogadro number and V the molar volume; σ_g is in effect a measure of the surface free energy of a mole of substance at the interface.

In treating our results in the same way, the question at once arises whether it is permissible to assign a relatively insignificant role to the quantity $\exp(-\Delta F_A/kT)$, for now we are dealing with liquids with polyatomic molecules where the transfer of a molecule from the liquid to the solid lattice may well be altogether more difficult than in the relatively simple metallic system. It is well known that, for this type of liquid, glass formation is by no means uncommon. We shall discuss this more fully in due course, but provisionally we will suppose that $\exp(-\Delta F_A/kT) \approx 10^{-2}$, the value used by Turnbull. We shall suppose that the average diameter of the drops is 50 microns; their size must in fact have varied considerably and may often have been less than this, but the values of σ are comparatively insensitive to n in equation (1), *i.e.*, to drop size. We suppose, moreover, that at the temperatures recorded in the Table at which spontaneous freezing may roughly be said to occur, the nucleation rate was 10^{-1} nuclei/second. With these assumptions $\Delta F_i^*/kT$ has to have a value of 62.

Summary of results concerning supercooling of liquids

	T_0 = m. p. (°K)	T_c = f. p. (°K)	Supercooling, $T_0 - T_c$ = ΔT	σ, ergs/cm.²	σ_g, cal./mole	$\sigma_g/\Delta H_f$	$\Delta T/T_0$
MeCl	175·6°	120 ± 1·5	55·6°	21·4	595	0·39	0·317
NH_3	195·5	155·2 ± 1·5	40·3	29·1	446	0·33	0·206
CCl_4 *a*	250·2	200·2 ± 2	50·4	6·67	280	0·47	0·202
CCl_4 *b*	250·2	200·2 ± 2	50·4	13·9	584	0·32	0·202
H_2O	273·2	232·7 ± 1	40·5	30·8	460	0·30	0·148
C_6H_6	278·4	208·2 ± 2	70·2	20·4	824	0·35	0·252
$Br{\cdot}[CH_2]_2{\cdot}Br$ ...	282·7	216·2 ± 2	66·5	21	835	0·33	0·235
Diphenyl	344	258 (?)	86	24·0	1260	0·31	0·25
Naphthalene ...	353·1	258·7 ± 1	94·4	30·1	1420	0·31	0·267
CBr_4 *a*	363·3	281 ± 5	82	10·7	458	$0{\cdot}48_5$	0·226
CBr_4 *b*	363·3	281 ± 5	82	21·8	934	0·34	0·226
$C_6H_5{\cdot}CO_2H$	395·0	275 ± 2	120	34·8	1480	0·36	0·304
White P_4	317·5	201·9	115·6	12·6	427	0·68	0·364

In the table there are presented values of σ derived from experimental ΔT values, and also calculated values of σ_g and of the ratio $\sigma_g/\Delta H_f$. It is interesting that for most of these liquids this last ratio is roughly constant, having a value of about 1/3. For carbon tetrachloride and tetrabromide two sets of figures have been given. This is because each of these substances undergoes a transition with a considerable entropy change at a higher temperature than that at which the supercooled liquid was observed to freeze. The figures marked "*a*" have been calculated on the assumption that this crystallisation produces the metastable high-temperature form; and those marked "*b*" have been estimated by assuming that the stable low-temperature form appears. In the latter calculation we have inserted for the latent heat quantity in equation (2) the value obtained by multiplying the m. p. by the sum of the entropies of fusion and transition. It is interesting that it is for the second alternative that the ratio is near 1/3. Calculations have also been made from Hildebrand and Rotariu's data (*J. Amer. Chem. Soc.*, 1951, **73**, 2524) on the supercooling of white phosphorus, which was studied by observing small drops on glass surfaces. If we suppose that at the lowest temperature to which the drops could be cooled and still remain liquid, the nucleation rate was the same at that assumed above, then the $\sigma_g/\Delta H_f$ ratio is now much greater than for any of the other liquids we have investigated (see table).

We may note that attempts have been made to explain the rough constancy of the ratio of the molar surface energy ($\sigma_M - T \,.\, \mathrm{d}\sigma_M/\mathrm{d}T$) of a normal *liquid* to its molar heat of *vaporisation*, which is usually between $\frac{1}{2}$ and $\frac{1}{4}$ (Skapski, *J. Chem. Phys.*, 1948, **16**, 389; Rideal, "Surface Chemistry," p. 30, Camb. Univ. Press, 1930). A difficulty arises in attempting to apply these ideas to our problem since σ_g is the molar interfacial *free* energy, and we have no means of measuring the interfacial energy. However, as now we have solid surface in contact with liquid it is possible that the entropy contribution is very small, because though the surface of the solid will to some extent be disordered this may be more or less balanced by an increased ordering of the liquid surface in contact with it. We may then take σ_g as being approximately the same as the surface energy. Since a molecule in the surface may be regarded as partly in the liquid one might expect σ_g to be of the order of one-half the latent heat of fusion. At least, therefore, we may describe our values for $\sigma_g/\Delta H_f$ as being not unreasonable. It is obviously desirable, however, to have more data for other liquids and it would be particularly valuable to have independent estimates for σ_g.

We may recall that our experiments with hydrogen sulphide and nitrous oxide suggested that with these liquids there was very little supercooling. We must stress that in the experiments with these substances it was difficult to produce clouds at all in a range of 20° or so below the m. p., but that those that were obtained always appeared to be frozen. When the substance is highly volatile under the conditions of the experiments, as these are, difficulties may be introduced by the speed with which distillation can take place which might lead to marked local cooling. But if the results are genuine then, since for neither of these liquids can ΔH_f be described as abnormally small, it follows that σ is relatively very low. The only physical property which appears to distinguish these liquids from any others is the high triple-point pressure (H_2S 174 mm.; N_2O 659 mm.).

We have already recalled that many organic liquids readily form glasses when cooled, and it seems worth while to consider briefly how this is to be interpreted. We should first point out that if ΔF_A of equation (1), which has been tentatively taken to be equal to the energy of activation for viscous flow, is put equal to zero, the nucleation rate has a maximum value at the relatively low temperature of $T_0/3$. If increasing positive values are assigned to ΔF_A the temperature of the maximum is displaced towards T_0. If the liquid can be supercooled to a temperature below the glass-transformation point T_g (roughly, this is really a comparatively narrow range of temperature over which the time of relaxation of those molecular motions which differentiate a supercooled liquid from its crystalline form become comparable with the time of an experiment), then it may be supposed that the liquid will never be observed to freeze spontaneously. Kauzmann (*Chem. Reviews*, 1948, **43**, 219) has pointed out that T_g is often near $\frac{2}{3}T_0$, and if we assume that $T_g \simeq \frac{2}{3}T_0$, it is of interest to enquire whether or not the viscosity term might reasonably be expected to prevent nucleation down to this temperature. At $\frac{2}{3}T_0$ [from equation (2)]:

$$\Delta F_i^*/\boldsymbol{k}(\tfrac{2}{3}T_0) = 72\pi\sigma^3/\lambda^2\boldsymbol{k}T_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Values of σ as determined above being used, this expression has a value of ~18 for water and ~28 for ammonia. This value should not differ widely from one substance to another and we will take it to be ~25. Now for nucleation not to occur in the drops considered above, ($\Delta F_i^*/\boldsymbol{k}T + \Delta F_A/\boldsymbol{k}T$) has to have a value greater than 67. [This value is derived from equation (1); for the drop size and rate of nucleation assumed above $r^*\boldsymbol{h}/n\boldsymbol{k}T \simeq e^{-67}$. From the equation it can be seen that $r^*\boldsymbol{h}/n\boldsymbol{k}T \simeq \exp\{-(\Delta F_A/\boldsymbol{k}T + \Delta F_i^*/\boldsymbol{k}T)\}$.] If therefore $\Delta F_A/\boldsymbol{k}T$ is ~42 at $\frac{2}{3}T_0$, spontaneous nucleation will be prevented.

ΔF_A being taken as not very different from the energy of activation for viscous flow, consideration of Barrer's data (*Trans. Faraday Soc.*, 1943, **39**, 48, 59) shows that a high value of $\Delta F_A/\boldsymbol{k}T$ at low temperatures is not unreasonable, especially for hydrogen-bonded and polymerised liquids. Values of $\Delta E_{\text{visc.}}/\boldsymbol{R}T$ for hydrogen-bonded liquids fall between about 4 and 15 at temperatures near the m. p.s, and when $\Delta E_{\text{visc.}}$ is large it increases rapidly as the temperature is lowered because of increasing structure in the liquid.

It may well be, of course, that ΔF_A corresponding to the free energy of activation of the transference of a molecule from the liquid to the solid is that for a rotational or reorientational movement and cannot, as we have hitherto supposed, really be identified with the activation energy for viscous flow. Smyth (*e.g.*, Baker and Smyth, *J. Amer. Chem. Soc.*, 1939, **61**, 2063) has called attention to the reluctance with which liquids crystallise when their molecules are roughly pear-shaped (*e.g.*, *iso*amyl bromide). Here, reorientational movement may be necessary for crystal growth but not for viscous flow, and the resistance to reorientation may increase more rapidly than that to the movement required for flow. In this connection we may recall that transitions in solids at which molecules gain orientational freedom are often co-operative, and we would except that for liquids also, as the temperature falls and reorientation becomes more difficult, the associated free energy increase rises rapidly. In this way we can understand that with falling temperature $\exp(-\Delta F_A/\boldsymbol{k}T)$ would decrease so rapidly that, notwithstanding the very rapid increase in $\exp(-\Delta F_i^*/\boldsymbol{k}T)$, the nucleation rate never reaches a sufficiently high value for crystallisation due to homogeneous nucleation to occur.

It will be remembered that our experiments with dioxan, *p*-xylene, *cyclo*hexane, and hydrogen chloride failed to show that freezing occurred in a narrow temperature range. This *may* have been due to glass formation, and it is interesting that there is evidence that *cyclo*hexane can form a glass (cf. Phibbs and Schiff, *J. Chem. Phys.*, 1949, **17**, 843); but we cannot be sure of this until further experiments have been performed.

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