Further Studies of the Supercooling of Drops of Some Molecular Liquids.

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Further experiments have been carried out on the extent to which liquid drops may be supercooled, by observation of clouds of droplets in a beam of light at different temperatures. For seven of the 21 liquids examined, it was possible to determine T_c, the mean temperature of the comparatively narrow range in which freezing appeared to start in these circumstances. For these liquids, values of the interfacial free energy between crystal and liquid have been derived, and compared with previous results. Some remarks are made on the possible reasons for failure to observe crystallisation in experiments of this kind.

This paper is a sequel to that of Thomas and Staveley (*J.*, 1952, 4569), describing experiments on the supercooling of various molecular liquids. Each liquid was examined as a cloud of small droplets. The cloud was produced at a temperature below the melting point, and examined in a beam of light. Frozen droplets scintillated, but if the cloud had a diffuse appearance the droplets were assumed to be still liquid. In this way it was established that, in the absence of heterogeneous catalysts, molecular liquids supercool very considerably before freezing.

We present here the results of further experiments of this kind carried out on 21 liquids, mostly having lower melting points than those examined previously. As in the earlier work, it was not possible to obtain conclusive results with every liquid, and for only seven of the 21 investigated were values for the degree of supercooling determined. We shall later briefly consider possible reasons for this.

EXPERIMENTAL

All the experiments described here were carried out with the all-glass apparatus shown in Fig. 3 of Thomas and Staveley's paper. A preliminary investigation of ammonia and carbon tetrachloride, which had been studied by these workers, gave results for the degrees of supercooling identical with those previously reported. In choosing the new liquids, it was desirable that they should have small or fairly symmetrical molecules, so that the chances of glass formation should be reduced, that they should not attack glass, grease, or mercury, and that the m. p.s and latent heats of fusion should be known. For most of the liquids examined, the melting points were below −80° c, and for almost all others it was very unlikely that a cloud of droplets would freeze above this temperature. Accordingly, it was not possible to employ the technique of seeding with solid carbon dioxide, which Thomas and Staveley used for liquids of higher m. p., to decide whether or not a cloud was frozen.

Great care was always taken to dry each sample thoroughly. For the first experiments with any one liquid it was not intensively purified. Further purification was, however, carried out before the final experiments when it appeared that positive results could be obtained, but this never produced any significant change in behaviour. This agrees with the earlier conclusion that the supercooling is not in any way critically dependent on the concentration of homogeneous impurities, unless these, by separating out and solidifying (as water might do), virtually act as heterogeneous catalysts.

We shall first summarise the results for those liquids for which positive conclusions were reached about T_c, the mean temperature of the comparatively narrow range in which freezing was observed to begin. The figure in parentheses after the name of each substance is its m. p. (in ° k).

Methyl Bromide (179·4°).—The final sample was purified by a double fractionation, and the value obtained for T_c was 155·0° ± 2° k. At or slightly below T_c frozen clouds scintillated spectacularly, and indeed this substance would serve very well for demonstration purposes. It is interesting to note, however, that if the cloud was produced at temperatures 15° or more below T_c no scintillations were visible. We do not know whether this was because at these lower temperatures the drops were frozen, but were too small to twinkle visibly, or because they had supercooled to glass, but this observation shows that it is desirable, in investigating a new substance, to make the temperature intervals between experiments fairly small.

Boron Trifluoride (144·5°).—T_c was established without difficulty as 126·7° ± 1·5° K, a sample purified by a double fractionation being used.

cyclo*Propane* (145·8°).—A sample of this substance for anæsthesia was further purified by fractionation in a column of the type described by Clusius and Riccoboni (*Z. physikal. Chem.*, 1938, *B*, **38**, 81); T_c was 128·0° ± 1·5° K. Between ~120° K and 128° K a cloud started to scintillate about a minute after its formation. Below ~120° K the clouds may best be described as apparently consisting of snowflakes rather than of individual crystals.

Thiophen (234·95°).—The final experiments were carried out on a constant-boiling fraction taken from a 12-plate column, and gave $T_c = 184·2° \pm 2·5°$ K. Between the production of the cloud and the appearance of scintillations, there was always a delay of 2—3 min. in the 10° interval below T_c. This, combined with the fact that the clouds were rather thin, made the uncertainty in T_c somewhat larger than for the three substances already dealt with. No scintillations were observable below 175° K.

Chloroform (209·7°).—The final sample was prepared by fractionating chloroform which had been washed with water and dried (P_2O_5); T_c was found to be 157·2° ± 2° K. Here again there was a delay between the formation of a cloud and the appearance of scintillations, of about 2 min. Scintillations were only observable a few degrees below T_c. Below ~118° K the appearance of a cloud was that of a snow-storm, as with *cyclo*propane at the lower temperatures, but with much larger flakes.

Sulphur Dioxide (197·64°).—The sample used was taken from a siphon and dried (P_2O_5) but not fractionated. The figure obtained for T_c was 164·5° ± 3° K, but the result was less definite than those just reported. Above ~165° K, all clouds had the appearance of fine drizzle and settled relatively rapidly. At very low temperatures the appearance of a cloud was like that of a snow-storm. As the temperature approached T_c, the flakes became smaller, but occasional scintillations were seen.

Methylamine (179·7°).—This was prepared by dropping an aqueous solution on to potassium hydroxide. It was dried first over potassium hydroxide and then over sodium, and finally fractionated in the low-temperature column. As with sulphur dioxide, the result is not free from ambiguity; but we consider that T_c is approximately 144° ± 5° K, since above the upper limit of this range, scintillations were never observed whereas they were seen below it, although only after a delay of 2—3 min. At still lower temperatures, scintillations were not seen.

For the following substances it was impossible to determine a value for T_c.

Krypton (115·95°).—It was disappointing that we were unable to measure T_c for this substance, since it would be particularly valuable to have a result for a monatomic liquid. An experimental difficulty was that the clouds were at best very thin. The triple-point pressure is nearly 1 atm., and consequently in the range in which T_c might lie a considerable quantity of vapour was required to saturate the cloud chamber. However, pre-charging of the cloud chamber to a pressure not quite sufficient to cause condensation did not result in an appreciably thicker cloud. By using liquid air as refrigerant, experiments were made down to 81° K. Scintillations could be observed at all temperatures from here to the m. p. These, however, only appeared after a lapse of time, but the crystals always came from the direction of the walls of the vessel, so it was likely that they originated on the surface.

Carbon Dioxide (m. p. 216·6° K; sublimation temp. at 1 atm. 194·8° K).—This substance was deliberately chosen since of all common substances it has the highest triple-point pressure. It was impossible to obtain clouds by any means above 191° K. All the clouds produced below this temperature appeared frozen, consisting either of scintillating particles or large white lumps, except at very low temperatures where the clouds had a diffuse appearance.

cyclo*Pentane* (179·4°), n-*Heptane* (182·5°), *Toluene* (177·7°), *Pyridine* (231·1°), *Tetramethylsilicon* (174·1°), *Tetramethyltin* (218·4°), *Silicon Tetrachloride* (205·5°), *Methylene Dichloride* (176·4°), *Methyl Alcohol* (176·3°), *Carbon Disulphide* (161·1°), *Ethylene Oxide* (160·6°).—No scintillations were observed for any of these substances at any temperature down to 95° K, although experiments were carried out at intervals which never exceeded 7° and were less where freezing might have been expected. Apart from the general tendency for clouds to be thicker and more diffuse at lower temperatures, there was never any more or less abrupt change in their appearance.

With toluene, at least, the failure was not surprising, since it could readily be supercooled to a glass in bulk. It seemed curious that a negative result was obtained for carbon disulphide. Glass formation does not seem at all likely with this substance But although it was examined particularly carefully, no sign of freezing whatever was seen. With pyridine the clouds were rather thin at the higher temperatures. Seeding with solid carbon dioxide had no effect.

Ethylene (103·7°).—This gave no indication of crystallisation down to 81° K, the lowest temperature that could be reached.

DISCUSSION

For the seven liquids for which it was possible to measure T_c, we have calculated the values of the quantities σ_g and $\sigma_g/\Delta H_f$, where ΔH_f is the heat of fusion in cal./mole, and σ_g is the surface free energy of a mole of the substance at the crystal–liquid interface. In these calculations, the results of which are given in the Table, Turnbull and Fisher's expression for the rate of homogeneous nucleation (*J. Chem. Phys.*, 1949, **17**, 71) has been used, and the same assumptions have been made as by Thomas and Staveley (*loc. cit.*). For methyl bromide and boron trifluoride, which have transitions near the m. p., the latent heat of fusion has been replaced by the product of the m. p. and the sum of the entropies of fusion and transition. This supposes that at T_c these substances crystallise in the form stable at that temperature (cf. results for carbon tetrachloride and carbon tetrabromide in the earlier paper).

	M. p., T_0 (° K)	T_c (° K)	Supercooling ($T_0 - T_c$)	σ_g, cal./mole	$\sigma_g/\Delta H_f$
Boron trifluoride...	144·5	126·7	17·8°	270	0·23
*cyclo*Propane	145·8	128·0	17·8	287	0·23
Methyl bromide ...	179·4	155·0	24·4	350	0·25
Methylamine	179·7	144	35·7	448	0·31
Sulphur dioxide ...	197·6	164·6	33·0	480	0·27
Chloroform	209·7	157·2	52·5	723	0·32
Thiophen	234·9	184·2	50·7	453	0·37

Although the seven values of $\sigma_g/\Delta H_f$ recorded in the Table are in the neighbourhood of one-third, like those for the molecular liquids previously studied, it is interesting that some of them are lower than any hitherto obtained, and that for three of the liquids concerned (methyl bromide, *cyclo*propane, and boron trifluoride), for which the determinations of T_c seemed particularly satisfactory, the melting points are also relatively low. This suggests the possibility, which can only be adequately tested by further experimental work, that there may be some rough correlation between $\sigma_g/\Delta H_f$ and T_0, the melting point, such that $\sigma_g/\Delta H_f$ is smaller the lower T_0. Admittedly, for methyl chloride (for which T_0 is only 4° different from that of methyl bromide), Thomas and Staveley found a rather higher value for $\sigma_g/\Delta H_f$ (0·39), but the determination of T_c for this substance was somewhat uncertain.

It seems desirable to emphasise that these estimates of σ_g depend on assumptions which must in principle represent approximations to the real state of affairs. First, T_c must depend on drop-size and we have made no attempt to measure this. But it is unlikely that this dependence is very sensitive, and since supercooled clouds of different substances produced by the same technique in the same apparatus persist for about the same length of time (a matter of minutes), it seems unlikely that there is any significant variation in drop size. It is less easy to judge the effect of two further assumptions, namely, that σ_g and the entropy of fusion are independent of temperature. From what is known about the relationship between surface tension and temperature, it is unlikely that σ_g would change rapidly. As for the entropy of fusion, experiments on substances such as glycerol and alcohols have shown that at very low temperatures the entropy difference between the glass and the crystal is only about one-half to one-third of the entropy of fusion at the melting point. The entropy difference between the supercooled liquid and the crystal decreases right from the melting point. Although glycerol and alcohols, by·virtue of their association, are rather exceptional liquids, we would expect a similar trend on the part of the entropy of fusion for molecular liquids in general, but unfortunately the information available is meagre. Lastly, as Thomas and Staveley pointed out, there is some ambiguity attending the value of the quantity $\exp(-\Delta F_A/kT)$, where ΔF_A is the free energy of activation for the actual process of addition of a molecule to a growing crystal nucleus. We have taken a value of 10^{-2} for this, and indeed if ΔF_A is identified with the value of $\Delta E_{\text{visc.}}$ (the activation energy for ordinary viscous flow) at room temperature, this exponential is not far from 10^{-2}. Unfortunately, for many of the liquids studied, viscosity data do not extend much below room temperature, and in any case we are concerned with the state of affairs well below the melting point. Pryde and Jones (*Nature*, 1952, **170**, 685) have recently succeeded in preparing water in a vitreous condition, and in measuring the temperature at which its molecules had acquired sufficient mobility to enable the glass to crystallise (144° K). From this they concluded that at this temperature, $\Delta E_{\text{visc.}}$ is at least 16,000 cal./mole, which is more than three times its value at the melting point. Similar large increases in $\Delta E_{\text{visc.}}$ are shown by supercooled alcohols.

Observations of this kind suggest that values of $\exp(-\Delta F_A/kT)$ in the neighbourhood of T_c may be much smaller than 10^{-2}, and the true values for σ_g consequently different from those calculated by us. In addition, they strengthen the possibility that the apparent failure of some liquids to freeze may be because homogeneous nucleation is prevented by a high value of ΔF_A. For toluene there is little doubt that this is so, since, as already mentioned, it can be supercooled to a glass in bulk. An interesting contrast is provided between *cyclo*pentane, *cyclo*hexane, *cyclo*propane, and benzene, since the two which were observed to crystallise are those with planar molecules. If, as seems likely, the process of addition to a growing nucleus is one involving molecular reorientation, rather than displacement, this reorientation might well be energetically more difficult for non-planar than for planar molecules. Likewise, the failures with silicon tetrachloride, tetramethylsilicon, and tetramethyltin, as contrasted with the ready crystallisation of carbon tetrachloride and carbon tetrabromide, may be ascribed to the fact that the very compact molecules of the last two compounds can readily reorientate themselves, whereas the greater length of the bonds radiating from the central atom in the molecules of the other three substances causes greater interlocking, and hence reduced rotational freedom.

Thomas and Staveley were not able to establish T_c for hydrogen sulphide, nitrous oxide, and hydrogen chloride, and we likewise did not succeed with krypton and carbon dioxide. These are all substances of high triple-point pressure and relatively low melting point. For a series of substances with the same values of $\sigma_g/\Delta H_f$, the degree of supercooling, $T_0 - T_c$, decreases as the melting point, T_0, falls. Moreover, if as tentatively suggested on p. 226, $\sigma_g/\Delta H_f$ itself tends to fall as T_0 decreases, $T_0 - T_c$ would be even less for lower-melting substances. Consequently, for the five gases under discussion, T_c may not be far below T_0. This, combined with the difficulty of producing clouds at all near the melting point, may have been responsible for our inability to determine T_c.

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