Fig. 1. Threshold of nucleation in supercooled liquids. ○, Molecular compounds (Staveley *et al.*, refs. 2 and 3); ◐, alkali halides (Buckle and Ubbelohde, refs. 4 and 5); ●, metals (Turnbull and Cech, ref. 1, and Turnbull, ref. 8)

ture $\theta = T_s/T_f$. Recent results for alkali halides^{4,5} show that for these compounds $\theta \sim 0.85$. In all these experiments the observation time was about 10 sec. irrespective of drop size. Collectively the results indicate a value of θ close to 0.82 (Fig. 1).

The parallelism between T_s and T_f , which extends over a very large range of temperature, does not seem to have been previously noted. It suggests some underlying connexion between the irreversible transformation of liquid to solid at the freezing point and the stable co-existence of these phases at the melting point. The value $\theta = 0.82$ refers to the quite arbitrary limitations of present methods of observing nucleation. It therefore appears likely that θ will be constant at any given nucleation-rate.

In view of current interest in the problem of liquid structure it seems important to point out that the constancy of θ also shows that the sizes of crystal nuclei, as measured by the number of molecules g^* comprising them, are the same to within an order of magnitude for all the compounds examined. The specific rate of nucleation in supercooled liquids may be written⁶:

$$J = K \exp(-\Delta\Phi^*/kT) \text{ sec.}^{-1} \text{ cm.}^{-3}$$

where $\Delta\Phi^*$ is the free energy of nucleation and K is a factor which is relatively insensitive to temperature for liquids which do not form glasses. By specifying the rate J the values of both θ and $\Delta\Phi^*/kT$ are determined for any such liquid. For the nucleation threshold, therefore:

$$\Delta\Phi^*/kT_s = \ln(K/J_s) = c_s \text{ (a constant);}$$

$$\Delta\Phi^* = c_s \theta kT_f$$

Assuming that a crystal nucleus is adequately described by a simple model of the Volmer type⁷:

$$g^* = 2\Delta\Phi^*/\Delta\psi$$

where $\Delta\psi$ is the decrease of free energy per bulk molecule. By means of the relation⁴:

$$N\Delta\psi = \theta\Delta S_f$$

where ΔS_f is the molar entropy of fusion, the following expression is obtained for the number of molecules in the threshold nucleus:

$$g_s^* = 2c_s R \theta / [(1 - \theta)\Delta S_f]$$

As c_s is roughly 60 (refs. 2, 4 and 8) a rule of thumb is:

$$g_s^* \sim 1,000/\Delta S_f$$

Metallic nuclei contain 200–400 atoms, while for molecular compounds g_s^* is mostly less than 200. Previous estimates of g_s^* for alkali halides⁴ were based on inadequate fusion data. Recent determinations⁸ of entropies of fusion show that the nuclei contain about 300 ions.

E. R. BUCKLE

Department of Chemical Engineering,
Imperial College of Science and Technology,
London, S.W.7.

¹ Turnbull, D., and Cech, R. E., *J. App. Phys.*, **21**, 804 (1950).

² Thomas, D. G., and Staveley, L. A. K., *J. Chem. Soc.*, 4569 (1952).

³ De Nordwall, H. J., and Staveley, L. A. K., *J. Chem. Soc.*, 224 (1954).

⁴ Buckle, E. R., and Ubbelohde, A. R., *Proc. I.U.P.A.C. Symp. on Thermodynamics* (1959).

⁵ Buckle, E. R., and Ubbelohde, A. R. (to be published).

⁶ Turnbull, D., and Fisher, J. C., *J. Chem. Phys.*, **17**, 71 (1949).

⁷ Dunning, W., "Chemistry of the Solid State", ed. by Garner (Butterworths, London, 1955).

⁸ Turnbull, D., *J. App. Phys.*, **21**, 1022 (1950).

⁹ Dworkin, A. S., and Bredig, M. A., *J. Phys. Chem.*, **64**, 269 (1960).

Self-Quenching Geiger Counters containing Mixtures of Permanent Gases

IN a recent communication, Collinson, Demetso-poulos, Dennis and Zarzycki¹ refer to a paper of mine² as negating the earlier work of Shore³.

My paper, it is true, reports the failure of a mixture composed according to Shore's prescription, but it also states that xenon-oxygen fillings worked very well if a low oxygen content was chosen. Besides that, the paper says that no harm was done even by a continuous discharge, running for 1 hr. at 50 μ amp. The startling quenching mechanism was explained by me as due to a certain resonance phenomenon, which had been found by the spectroscopists⁴ and which occurs at very low oxygen contents only.

Perhaps the addition of nitrogen or argon results in a still unknown, but no less effectual mechanism, even at higher oxygen contents. Only by 'burning out' in a continuous discharge, however, can it be certain that no unintentional admixture of other gases or vapours provokes self-quenching behaviour in apparently pure permanent gases, as discovered by Bosch⁵.

OSWALD RIEDEL

Badische Anilin- und Soda-Fabrik AG.,
Ludwigshafen a. Rh.,
Germany.

¹ Collinson, A. J. L., Demetso-poulos, I. C., Dennis, J. A., and Zarzycki J. M., *Nature*, **185**, 369 (1960).

² Riedel, O., *Z. Naturforsch.*, **5**, a, 331 (1950).

³ Shore, L. G., *Rev. Sci. Instr.*, **20**, 956 (1949).

⁴ Kenty, C., Aicher, I. O., Noel, E. B., Poritsky, A., and Paolino, V., *Phys. Rev.*, **69**, 36 (1947).

⁵ Bosch, C., *Ann. Physik*, **19**, 65 (1934).

WE feel that the xenon-oxygen phenomenon referred to by Dr. Riedel, although interesting, is only of importance in mixtures where xenon is the main gas. While such an effect is possibly a small contributory factor in the quenching mechanism of the argon-xenon-oxygen-nitrogen mixtures which we have investigated, our results show that the important mechanism is the interaction of xenon with argon metastable states.