

For some time I have been examining the effect of substituting the absolute value of a transition point for T in the melting point formula, and have obtained interesting results. Taking 848°K . as the transformation temperature of α , β -quartz, the corresponding frequency is 4.09×10^{12} sec.⁻¹ or 136 cm.⁻¹. This is very nearly the same as the Raman line 132 cm.⁻¹.

The two suggestions which I wish to emphasize are these: (1) the occurrence of a transformation is associated with some kind of resonance between approximately equal frequencies characteristic of the phases concerned; (2) the applicability of the Sutherland-Lindemann melting point formula to the transition point.

H. S. ALLEN.

University,
St. Andrews.
Feb. 7.

Chemical Action of γ -Radiation from ^{80}Br

DURING the course of an investigation into the exchange of radiobromine between a number of organic and inorganic bromides, it has been observed that with certain of the latter, for example, aluminium bromide, and a wide variety of organic bromides, a complete exchange of all the bromine atoms in the system takes place very quickly at room temperature. With many other inorganic bromides, however, there is apparently no exchange, but an extraction of the 18-min. ^{80}Br isotope from the radioactive organic bromide.

For example, if inactive antimony tribromide be dissolved in radioactive ethyl bromide several hours after the preparation of the latter, that is, when all the 18-min. isotope originally present has decayed, and immediately after the dissolution the ethyl bromide be volatilized away *in vacuo*, the residue of antimony tribromide is found to be strongly radioactive, with a half life of 18 min., the 4.5- and 36-hour periods being found in the condensed ethyl bromide.

That is, the antimony tribromide has made a selective extraction of the short-lived radiobromine isomer which has grown from, and is in transient equilibrium with, the parent 4.5-hour ^{80}Br . This result is to be attributed to a form of intramolecular photo-dissociation of the ethyl bromide by the internal conversion of the γ -ray which, as Snell¹, Abelson² and others have shown, is emitted by the bromine nucleus during the isomeric transition. A similar extraction was observed with arsenic tribromide, phosphorus pentabromide and, though the amount extracted was less, with crystals of mercuric bromide and of potassium bromide, and with metallic silver, mercury and even gold. In each case the radiobromine extracted was almost pure 18-min. ^{80}Br , the 'tail' to the decay curve due to the longer-lived isotopes being very small—generally less than 1 per cent of the total initial activity.

Segré, Halford and Seaborg³ obtained a partial separation of the radiobromine isotopes by the precipitation of silver bromide from an aqueous methyl alcoholic solution of radioactive *tert*-butyl bromide, and DeVault and Libby⁴ obtained a more complete separation by the precipitation of silver bromide from a radioactive bromate solution. These authors attributed the separation to a chemical activation of the molecule containing the bromine, by the recoil

from an internal conversion electron. LeRoux, Lu and Sugden⁵ have also found that a greater proportion of the 18-min. isomer than of the 4.5-hour isomer can be extracted by aniline from neutron irradiated ethylene dibromide, or by water from a benzene solution of a radioactive alkyl bromide, and offer as explanation⁶ that the soft γ -ray gives a recoil which can only activate, but not disrupt, the C-Br bond.

The present results indicate, however, at all events in the case of ethyl bromide, that the process is not simply a matter of supplying an extra activation energy (over that received spontaneously by thermal agitation) to an otherwise exothermic reaction, since the removal of a bromine atom or ion from an ethyl bromide molecule by arsenic tribromide or mercuric bromide, for example, is endothermic by a very large amount.

Moreover, the mechanical recoil of the bromine nucleus from the γ -ray or from a conversion electron cannot be a major factor in these reactions. Siday⁷ has shown that the energy of this γ -ray emitted during the transition is about 43,000 e.v. The energy of recoil of the comparatively heavy bromine nucleus from such a γ -ray is about 286 cal./mol., which is less than the energy of thermal agitation of the molecule at room temperature. The internal conversion of this γ -ray results in the expulsion of conversion electrons, the recoil from which will be greater than from the γ -ray, but even with 100 per cent efficiency of recoil would be less than 7 kcal./mol. Such an additional energy would accelerate the hydrolysis of an alkyl bromide, but could not bring about the present results. These suggest that a bromine atom or ion is broken completely away from the ethyl bromide molecule before reaction, a process requiring about 60 kcal./mol. if the disruption is into neutral fragments, and rather more for disruption into ions (much of the additional energy required to form the ions is recovered as solvation energy when the process takes place in solution).

It appears more probable, therefore, that the C-Br bond is broken immediately following the nuclear transition, not by mechanical recoil of the bromine atom, but by a process involving any one of a series of excited molecular states which are produced during the gradual settling down of the bromine atom after the start of the internal conversion. That is, the molecule is broken up, not merely activated, by a process which is more in the nature of a photo-dissociation brought about by intramolecular quanta.

All these reactions were carried out with anhydrous materials at room temperature, the ethyl bromide being volatilized away *in vacuo* ($\sim 10^{-3}$ mm. mercury), at or below room temperature and condensed by liquid air. The radiobromine was converted into AgBr, the activity of which was measured with a Lauritsen type quartz fibre electroscope.

F. FAIRBROTHER.

Department of Chemistry,
University of Manchester.
Feb. 2.

¹ Snell, *Phys. Rev.*, **52**, 1007 (1937).

² Abelson, *Phys. Rev.*, **56**, 753 (1939).

³ Segré, Halford and Seaborg, *Phys. Rev.*, **55**, 321 (1939).

⁴ DeVault and Libby, *Phys. Rev.*, **55**, 322 (1939).

⁵ LeRoux, Lu and Sugden, *NATURE*, **143**, 517 (1939).

⁶ Lu and Sugden, *J. Chem. Soc.*, 1273 (1939).

⁷ Siday, *NATURE*, **143**, 681 (1939).