



Fig. 1. Relationship between thermal expansion and rank of coal

It should be noted that the expansion coefficient appears to be even better related to the volatile matter than to the carbon content.

The results are shown graphically in Fig. 1. The broken line has been calculated from the results of Schuyer and van Krevelen¹ for expansions perpendicular and parallel to the bedding plane, assuming the expansion to be isotropic in the latter plane. The agreement between the two main sets of independent observations is better than usually expected for measurements on coals of different origin. The values found by Macrae and Ryder² refer only to the expansion parallel to the bedding plane and are too large to be included on this graph; but it is interesting to note that the different results obtained by them for two samples of the same coal, measured parallel to the bedding plane, could mean that anthracite is anisotropic in all three major planes. This is not well supported, however, by the agreement, already mentioned, between the mean coefficients obtained by direct observation of the cubical moduli and those calculated from the separately measured parallel and perpendicular moduli.

A full description of the apparatus, and a discussion of the results will appear elsewhere.

This work forms part of the programme of research of the Fuel Research Board of the Department of Scientific and Industrial Research, and is published by permission of the Director of Fuel Research.

A. S. JOY

Fuel Research Station, River Way,
London, S.E.10. Aug. 21.

¹ Schuyer, J., and van Krevelen, D. W., *Fuel*, **34**, 345 (1955).

² Macrae, J., and Ryder, C., *Nature*, **176**, 265 (1955).

³ Bangham, D. H., and Franklin, R. E., *Trans. Farad. Soc.*, **42B**, 289 (1946).

Separation of Ions at Crystallization of Water

ACCORDING to Workman and Drost-Hansen¹, a substantial amount of fluorine ions is incorporated into ice if it is crystallized from diluted solutions of caesium fluoride. We have studied this process further, and found that it is not fluorine ions which are incorporated into ice but rather electrically neutral molecules of hydrogen fluoride.

One half of a diluted solution of caesium fluoride in water was frozen and the ice separated from the remaining liquid. The water used had been distilled in a vacuum and was free of impurities, especially

Table 1

Sample	mol. F'/l.	pH	F' (mgm./10 cm. ³)
Original solution	5.82×10^{-3}	8.0	1.105
Non-frozen liquid	8.42×10^{-3}	8.5	1.658
Ice	9.7×10^{-4}	7.0	0.184

carbon dioxide. The pH of the remaining liquid was found to be higher than that of the thawed ice. An example is given in Table 1.

The accuracy of these measurements was not very high because the determination of the pH-value was carried out by means of an indicator. We are now carrying out more precise measurements.

The above experiments agree with results on the incorporation of hydrogen fluoride into ice. We found that small quantities of hydrogen fluoride can be built into the ice lattice. According to previous investigations², ammonium fluoride forms mixed crystals with ice in a range up to about 10 per cent ammonium fluoride. The replacement of water molecules in ice by ammonium fluoride seems to be facilitated by the fact that the ratio H/(N+F) is the same as the ratio H/O in water. Since, if water molecules are replaced by hydrogen fluoride, this ratio is smaller than 2:1, a greater disturbance by missing hydrogen bonds is introduced if water is replaced by hydrogen fluoride. This exemplifies the great influence of hydrogen bonds on the stability of the ice lattice.

This investigation was carried out under a contract of the Snow, Ice and Permafrost Research Establishment, Corps of Engineers, U.S. Army.

R. BRILL
H. ENDER

Physics Department,
Polytechnic Institute of Brooklyn,
Brooklyn 1, New York. June 22.

¹ *Phys. Rev.*, **94**, 770 (1954).

² Brill, R., and Zaromb, S., *Nature*, **173**, 316 (1954).

Magnetic Catalysis of the Decarboxylation of Oxaloacetic Acid

KINETIC studies of the decarboxylation of phenylmalonic acid in aqueous solution in the presence of high concentrations of rare-earth ions show that diamagnetic ions have little effect on the rate of reaction, while the paramagnetic dysprosium ion leads to an acceleration in rate of the order of 10 per cent^{1,2}. Rare-earth ions do not appear to become co-ordinated appreciably with phenylmalonic acid. Since any magnetic effect must be a very sensitive function of the distance between catalyst and substrate, a study is now being made of the kinetics of decarboxylation of an acid, the anions of which are known to become co-ordinated more strongly with metal ions.

The kinetics of decarboxylation of oxaloacetic acid and its anions have been investigated by Pedersen³. We have now measured the rates of decarboxylation of this acid in aqueous solution at 37° in the presence of lanthanum, gadolinium, yttrium, dysprosium and lutecium ions (Clayton, J. P., and Gelles, E., unpublished results). The manometric method⁴ employed for following the evolution of carbon dioxide yields first-order rate coefficients accurate to ± 3 per cent. pH measurements show that the thermodynamic dissociation constants (M^{3+}) (A^-)/(MA^+), where M^{3+} represents