

been lost in the other holes that no drill rods were available to progress farther. A continuation of the permafrost drilling programme is being carried out during the present summer, when it is hoped that the objective of 1,000 ft. will be reached.

The average conductivity of the bedrock as determined from the core samples by Prof. A. D. Misener, of the University of Western Ontario, London, Ontario, is:

$$K = 0.0066 \text{ c.g.s. units at } 31.2^\circ \text{ C.}$$

A thorough analysis has not been made as yet of the soil temperature observations from Resolute. Nevertheless, a number of interesting features has been noted.

(1) The temperatures at the 8-in. level show short-period fluctuations which reflect the fluctuations of the air temperature above the surface. However, these fluctuations from ambient air temperatures are rapidly damped out with increasing depth and are practically negligible at the 60-in. level.

(2) There is a marked lag in seasonal temperature changes with depth. For example, the temperatures at the 8-in. and 18-in. levels reach a maximum about the second week in August, whereas the temperature at the 60-in. level continues to rise until mid-September. The temperatures from the surface to the 60-in. level fall at varying rates after mid-September, so that by the last week in September there is a reversal in sign of the temperature gradient.

(3) The temperatures in the layers near the surface begin to rise in early March, and about May 1 there is again a reversal in sign of the temperature gradient from the surface to the 60-in. level.

(4) From about August 25 to September 15, the temperatures within 18 in. of the surface remain near the freezing point, indicating that the complete freezing of the water in the active layer takes about three weeks.

(5) The temperatures at the 98-ft., 300-ft. and 450-ft. levels remain practically constant with the following values: 98 ft., -13.50° C. ; 300 ft., -11.59° C. ; 450 ft., -9.54° C.

(6) The layer from 50 ft. to 98 ft. is nearly isothermal.

(7) Seasonal temperature changes are perceptible to near the 50-ft. level; but the lag at this level amounts to about six months.

ANDREW THOMSON
(Controller of
Meteorological Services)
P. C. BREMNER

Department of Transport,
315 Bloor Street West,
Toronto 5. July 15.

Reaction between Diethyl Peroxide and Nitric Oxide

IN the hope of trapping the radicals probably produced during the photolysis of diethyl peroxide, the vapour of the latter was mixed with a several-fold excess of nitric oxide in a 3-litre 'Pyrex' bulb. The mixture was then passed through a water-cooled helical silica tube surrounding a mercury arc into a trap immersed in 'Drikold'. Suspiciously large amounts of ethyl nitrite were found in the trap, and even larger quantities were collected in a blank run without the arc. After the mixture had been stored in the dark for twenty-four hours, spectrophotometric

examination showed that a major portion of the peroxide had been converted into nitrite.

The inhibition by nitric oxide of the thermal decomposition of diethyl peroxide¹ is clearly no evidence for a free radical mechanism.

H. N. MORTLOCK
D. W. G. STYLE

King's College,
Strand,
London, W.C.2.
April 23.

¹Moriya, *Rev. Phys. Chem., Japan*, 143 (1946).

Inhibition of the Thermal Decomposition of Diethyl Peroxide

THE mechanism of the thermolysis of diethyl peroxide is uncertain. Harris and Egerton believed the reaction to be a straightforward, unimolecular decomposition, although they observed short induction periods with some samples and generally much longer ones in the presence of nitric oxide¹. The products suggest the occurrence of reactions involving free radicals, and in the opinion of Neumann² the decomposition is a chain reaction. It is, however, difficult to reconcile a significant participation of free radicals in the decomposition with the first-order kinetics and the low activation energy (c. 31 k.cal.), compared with accepted dissociation energies of O—O bonds (HO—OH, 54 k.cal.³, *t*.BuO—O*t*.Bu, 39 k.cal.⁴).

A re-examination of the reaction in a spherical 2-litre 'Pyrex' vessel using peroxide pressures of a few millimetres of mercury has, in the main, confirmed the results obtained by Harris and Egerton. Our velocity constants, derived from initial rates, were however about 25 per cent greater than those of Harris and Egerton, and the activation energy a little smaller. An appreciable reaction of zero order appeared to be superimposed on the first-order reaction at temperatures below 160° C. During the course of individual reactions, the first-order law was not well obeyed by the pressure change, and the energy of activation derived from the 'half lives' of the pressure change were considerably less than that obtained from the initial rates, and was, indeed, close to the value of about 22 k.cal. obtained by Russian authors⁵.

When hydrogen iodide was added to the peroxide vapour at c. 140° C., the rate of change of pressure was reduced and iodine was formed. Excess hydrogen iodide reduced the rate to zero. Addition of iodine also inhibited the pressure change, although not completely, a limit of about 40 per cent of the uninhibited rate being attained with excess iodine.

In view of the reaction observed with nitric oxide⁵, caution is required in the interpretation of these observations, which are being extended.

A. D. JENKINS
D. W. G. STYLE

King's College,
Strand,
London, W.C.2.
April 23.

¹*Proc. Roy. Soc., A*, 163, 1 (1938).

²Blat, Gerber and Neumann, *Acta Physicochim., U.R.S.S.*, 10, 273 (1939). Neumann and Tutakin, *Acta Physicochim., U.R.S.S.*, 9, 861 (1938).

³Giguere, *Canad. J. Res., B*, 28, 17 (1950).

⁴Rust, Seibold and Vaughan, *J. Amer. Chem. Soc.*, 72, 338 (1950).

⁵Mortlock and Style (see preceding communication).