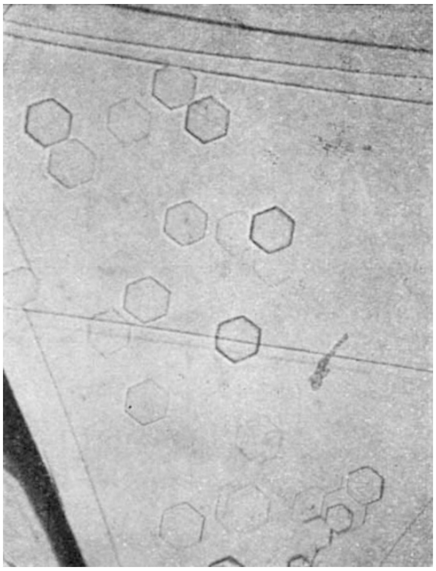

Fig. 2. Hexagonal etch pits of parallel orientation produced by atomic nitrogen on graphite crystal at 1,100° C. ×c. 130.

reactions are not obvious. The observed differences in the effects produced by atomic oxygen and atomic hydrogen may, however, be tentatively related to the differences in the surface mobilities of these absorbed species. Adsorbed oxygen atoms are believed immobile[3] and adsorbed hydrogen atoms exhibit high mobility on a carbon surface[6]. The behaviour observed here for nitrogen atoms strongly suggests that a mobile layer is involved during the attack on the graphite crystal surface.

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Vapour Pressure of $H_2{}^{18}O$ Ice (I) (—17° C to 0° C) and $H_2{}^{18}O$ Water (0° C to 16° C)

WE have measured the vapour pressure isotope effect (VPIE) between $H_2{}^{18}O$ and $H_2{}^{16}O$ ice from −17° C to 0° C and have obtained results in disagreement with those reported by Matsuo and Matsubaya[1]. In order to check our measurements we have also determined the VPIE in the liquid phase and obtained results in good agreement with Szapiro and Steckel[2]. Also we have calculated from the present data an ice–liquid fractionation factor

$$\alpha_{s/l} = (H_2{}^{16}O/H_2{}^{18}O)_{\text{liq}}/(H_2{}^{16}O/H_2{}^{18}O)_{\text{solid}} = 1{\cdot}0026 \pm 0{\cdot}0003$$

in good agreement with O'Neil's directly measured value of 1·0030 ± 0·0002 (ref. 3).

Our differential vapour pressure apparatus will be described elsewhere. The samples are contained in a common copper block whose temperature is controlled and measured to 0·001° C. We estimate that the temperature difference between samples is significantly less than 0·0002° C. The pressure differences are measured with a calibrated differential capacitance manometer. The vapour pressure of $H_2{}^{16}O$ water at each temperature can be obtained to sufficient accuracy for the present purpose from standard tables[4], but we have chosen to use a new theoretical relation derived by us which is substantiated by new measurements of the vapour pressure of $H_2{}^{16}O$ ice (results to be published shortly).

The 0·75 cm³ sample of $H_2{}^{18}O$ (H normalized) was kindly supplied to us by Dr G. Jakli of the Central Research Institute for Physics, Hungarian Academy of Sciences, Budapest. Their mass spectrometric analysis gave for oxygen, ${}^{18}O = 69{\cdot}0 \pm 0{\cdot}5$ per cent, ${}^{17}O = 1{\cdot}4 \pm 0{\cdot}2$ per cent, ${}^{16}O$ by difference. The deuterium concentration was only 1·03 ± 0·01 times normal abundance. The pressure differences were corrected to 100 per cent $H_2{}^{18}O$ assuming Raoult's law and the law of the geometric mean for $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$.

In the experiments 71 points were measured in the ice range, 0° C to −17° C, and 40 points in the liquid, 0° C to 16° C, over a ten day period. The two parameter least square fits are

$$\ln(R_{\text{solid}}) = \ln\left(\frac{P_{H_2{}^{16}O}}{P_{H_2{}^{18}O}}\right)_{\text{solid}} = \frac{2{\cdot}110}{T} + 0{\cdot}00656 \qquad (1)$$

$$256 < T < 273$$

$$\ln(R_{\text{liquid}}) = \ln\left(\frac{P_{H_2{}^{16}O}}{P_{H_2{}^{18}O}}\right)_{\text{liquid}} = \frac{13{\cdot}764}{T} - 0{\cdot}03872 \qquad (2)$$

$$273 \leq T \leq 289$$

The calculated logarithms are good to ±3 to 4×10^{-4} between 0 and −17° C, and to $\pm 2 \times 10^{-4}$ between 0 and 16° C. Our results for ice are thus consistently about 0·002–0·003 ln (R) units above those of reference 1, the only other reported measurements. In the liquid we calculate $\ln(R) = 0{\cdot}0090 \pm 0{\cdot}0002$ at 15° C in agreement with the value $\ln(R) = 0{\cdot}0097 \pm 0{\cdot}0003$ reported by Szapiro and Steckel[2] at the low temperature end of their measurements. Simultaneous solution of (1) and (2) at the melting point gives $\ln(\alpha_{s,l}) \approx \ln(R_{\text{solid}}) - \ln(R_{\text{liq}}) = 0{\cdot}0026 \pm 0{\cdot}0003$ in agreement with O'Neil's value of 0·0030 ± 0·0002. We are thus forced to conclude that Matsuo and Matsubaya[1] are some 20 per cent low in their value for $\ln(R_{\text{solid}})$ $(\alpha_{s,v})$. This is probably due to experimental difficulties arising from their extremely small (10 mg) samples.

A more complete report, including theoretical interpretation, will be submitted for publication in the near future. We acknowledge the financial support of the United States Department of Interior, Office of Water Resources Research, and the Petroleum Research Fund, American Chemical Society.

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