

which the temperature was allowed to rise at the same rate as in (B) but without sliding. Then sliding was carried out at the temperature indicated by the crosses. These curves coincide with the lower curve (B).

These experiments show that the appearance or non-appearance of friction temperature transitions in situations where En 31 is lubricated by mineral oil in low speed sliding experiments depends, among other things, on the rate of heating of the contact. The rapid heating experiments on run-in surfaces reveal friction-temperature transitions at moderate temperatures. These transitions are obscured by protective films formed during slow heating experiments. In the case of high speed heating experiments, the film did not form at a high enough rate (until about 140°C) to have any reducing effect on friction. The last set of experiments<sup>3,4</sup> and some preliminary work on reflexion infrared spectroscopy show that the film is formed thermally and oxidatively and not by some tribochemical process.

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- <sup>1</sup> Blok, H., *NASA Symposium Preprint*, **1**, 4.1 (1969).  
<sup>2</sup> Stafford, J. V., thesis, Univ. Reading (1971).  
<sup>3</sup> Barwell, F. T., and Milne, A. A., *Proc. Inst. Petrol.*, **35**, 455 (1949).  
<sup>4</sup> Grew, W., and Cameron, A., *Nature*, **217**, 481 (1968).

## Electrical Conductivity of Quartz

HYDROXYL ions diffuse slowly in silicas and motion of these ions through a quartz network, or the formation of defects for this motion, involves breaking silicon-oxygen bonds which have a bond energy of more than 100 kcalories mol<sup>-1</sup>. Thus it is unlikely that White<sup>1</sup> observed hydroxyl ion motion in quartz. His low activation energy of 13 kcalorie mol<sup>-1</sup> is closer to that for the motion of monovalent cations<sup>2</sup>.

The electrical conductivity of quartz or fused silica results from the motion of monovalent cations through the silicon-oxygen network<sup>3-5</sup>. This assertion is supported by ion exchange experiments, in which monovalent cations can be introduced into the silica from fused salts. No anions go into the quartz or fused silica in these experiments. The monovalent cations are associated with negatively charged aluminium ions in the silicon-oxygen network<sup>3</sup>. There are no positively charged groups that can accept monovalent anions.

White claims that the appearance of an OH absorption band in the near infrared in the diffused areas demonstrates that he observed hydroxyl ion motion<sup>1</sup>. These bands are, however, also augmented when hydrogen ions exchange for alkali ions in quartz<sup>3</sup>, forming -OH instead of -OX bonds (where X is an alkali ion).

Water diffuses as a molecule in fused silica<sup>6</sup>; these molecules react with the silica lattice to form SiOH groups, but these are very immobile, as is shown by the conductivity study of Garino-Canina and Priquelier<sup>7</sup>. Water diffuses much more slowly in quartz than in fused silica. Kats treated quartz crystals in water or D<sub>2</sub>O vapour at 1,000°C and found no increase in the OH bands that could be attributed to water diffusion<sup>3</sup>; he did see changes in these bands resulting from

exchange and interdiffusion of hydrogen or deuterium ions, and he calculated a diffusion coefficient of about  $2 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup> for exchange of these ions at 1,000°C.

It seems therefore quite likely that White was observing the motion of monovalent cations, including hydrogen ions, and not of hydroxyl ions.

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- <sup>1</sup> White, S., *Nature Physical Science*, **230**, 192 (1971).  
<sup>2</sup> White, S., *Nature*, **225**, 375 (1970).  
<sup>3</sup> Kats, A., thesis, Univ. Delft (1961).  
<sup>4</sup> Mortley, W. S., *Nature*, **221**, 359 (1969).  
<sup>5</sup> Doremus, R. H., *Phys. Chem. Glasses*, **10**, 28 (1969).  
<sup>6</sup> Doremus, R. H., in *Reactivity of Solids* (edit. by Mitchell, J. W., De Vries, R. C., Roberts, R. W., and Cannon, P.), 667 (Wiley-Interscience, New York, 1969).  
<sup>7</sup> Garino-Canina, V., and Priquelier, M., *Phys. Chem. Glasses*, **6**, 6 (1965).

## Reply to Doremus

DOREMUS implies that the hydroxyl ion diffusion which I observed<sup>1</sup> was in fact the result of the movement of monovalent cations, present as impurity ions in quartz. If this was so I was monitoring self-diffusion currents because I employed a platinum anode which was neither a source of alkali nor of hydrogen ions. The conductivity for a self-diffusion current decreases exponentially with time<sup>2</sup> whereas for an ionic current the conductivity<sup>3,4</sup> increases to a maximum constant value and therefore the one can be readily distinguished from the other. The currents I observed were of the latter type and the diffusing ions must have originated in the cathode. I used three different minerals, goethite, talc and kaolinite as cathodic sources of hydroxyl ions and observed a similar OH absorption band in the near infrared spectra of the quartz; I obtained a similar activation energy with each source. I did not detect an OH absorption band after self-diffusion experiments although this has been observed by others using a more sensitive infrared technique<sup>5</sup>.

I do not consider that an activation energy of 15 kcalories mol<sup>-1</sup> is unusually low for the diffusion of hydroxyl ions in either quartz or silica, even if the breaking of silicon-oxygen bonds is involved. Rybach and Laves<sup>6</sup> have shown a large increase (approximately ten-fold) in the number of sodium ions present in quartz after a sodium diffusion when compared with the number of monovalent cations present before the diffusion and also when compared with the aluminium ion content of the quartz. These excess sodium ions must be attached to broken silicon-oxygen bonds if the charge neutrality of the quartz is to be preserved. Silicon-oxygen bonds are therefore broken during the diffusion process. The activation energy recorded by Rybach and Laves<sup>6</sup> for the sodium diffusion was 24 kcalories mol<sup>-1</sup>, similar to that determined by other workers<sup>7</sup>, and not the 100 kcalories mol<sup>-1</sup> as envisaged by Doremus. McLaren and Retchford<sup>8</sup> have observed that dislocation movement, which because of the core structure of a dislocation in quartz<sup>9</sup> requires the breaking of silicon-oxygen bonds, has an activation energy of between 10 and 20 kcalories mol<sup>-1</sup> in hydrolytically weakened quartz. Thus, in the presence of certain ions—namely alkali, hydroxyl and protons—it appears that silicon-oxygen bonds in quartz are less stable than theoretically predicted.