

solution seem to be adequately described by Virk's limiting-velocity profile model<sup>4</sup>.

The bulk of turbulence production is associated<sup>6</sup> with low speed streaks which originate near the wall in the viscous sublayer and with their subsequent eruption or 'bursting'. From a study of the video records, measurements of the mean transverse spacing of the streaks,  $\lambda$ , the burst frequency per unit span,  $F$ , and the time between bursts,  $T_b$ , were determined (Table 1). The results obtained with water show fairly good agreement with previous investigations<sup>5-7</sup>. In addition to producing a large friction reduction the micellar solution showed a large increase in the transverse spacing of the streaks and a large reduction in the burst frequency. These changes are more dramatic than those found by previous investigators who used less effective drag reducing solutions<sup>7</sup>. Although the time between bursts  $T_b$ , is increased, the value still seems to correlate with the friction velocity,  $u^*$ , on the same unique line as that found with water and other polymeric solutions (ref. 7, and B. U. Achia and D. W. Thompson, unpublished).

The shape of the mean velocity profile supports the use of similarity laws for the prediction of boundary-layer skin friction in conditions of maximum drag reduction.

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## Carbon fibre pH-sensitive electrode

VARIOUS forms of carbon have been considered as possible indicator electrodes for use in locating end points in acid-base titrations; these forms have included graphite<sup>1</sup>, vitreous or glassy carbon<sup>2</sup> and pyrolytic graphite<sup>3</sup>. Microelectrodes can be used in titrations of small volumes, such as those found in biological cells<sup>4</sup>, and certain forms of carbon such as glassy carbon, are exceptionally resistant to oral and tissue fluids<sup>5</sup>. We have examined the electrical potential response of a single carbon fibre to pH changes in aqueous electrolyte solutions.

The potential of a carbon fibre electrode 1 cm long and 7–8  $\mu\text{m}$  in diameter, sealed into a Pyrex glass tube with epoxy resin, was measured against a saturated calomel reference electrode in various buffer solutions in the pH range 1–13, using a Corning EEL 109 digital pH meter used in its millivolt measuring mode. We found a linear relationship between the potential and pH, with a negative slope of about 50 mV per pH unit at room temperature (about 20 °C). The potential in any given buffer, such as 0.05 M potassium hydrogen phthalate, is stable to within 1 mV, within measuring times of a few minutes. Larger variations in potential (and also the slope factor) were, however, observed when the same electrode was examined over a period of weeks; this implies that a carbon-fibre pH electrode of this kind must be calibrated on each day of its use.

The potential of a carbon fibre pH electrode is unaffected by the presence or absence of dissolved oxygen: the same potential was recorded even when pure nitrogen was

bubbled through the buffer solution. A small negative shift in potential was, however, observed with temperature increase (about 0.6 mV °C<sup>-1</sup>). The potential of a carbon fibre electrode is affected by the presence in solutions of strong oxidants such as bromine and cerium(IV) and also by the presence of reductants, such as arsenic(III).

We believe that the observed pH response of the carbon fibre electrode may be caused by the possible ionisation of carboxylic acid groups formed on the surface of carbon by surface reactions with atmospheric oxygen<sup>6,7</sup>.

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## Electrostatic energy of columbite/ixiolite

A KNOWLEDGE of the crystal structure of an inorganic compound and the appropriate ionic charges is usually sufficient to allow the calculation of the electrostatic energy<sup>1-3</sup>. A more difficult situation is found in crystals where some or all of the cations are disordered so that on the average a particular cation site is occupied by two or more cations with different charges. Very accurate crystal structure refinements, often including refinement of site occupancies, can give a good description of the nature of the disorder and the average composition of each cation site. The electrostatic energy can then be calculated using the average ionic charges on each of the disordered sites. Such an approach has been used to compare the stabilities of ordered and disordered structures of pyrrhotite<sup>4,5</sup> and some complex niobium and tantalum oxides<sup>6</sup>. There seems no theoretical justification for the use of average cation charges for the calculation of the potential energy of a disordered crystal so such calculations must be treated with caution.

Consider a hypothetical crystal structure in which two different cations with different ionic charges occupy four cation sites such that, in the completely ordered arrangement, three are occupied by one ion (A) and the other site contains the second type of ion (B). The ordered arrangement then may be represented by the symbols AAAB. A completely disordered version of this structure determined from a diffraction experiment would be (as indicated above) 3/4A+1/4B for each of the four cation sites. But on the level of an individual unit cell, each cation can be either A or B only and not some fictitious average ion. There are four unique arrangements of 3A and 1B over four sites, namely AAAB, AABA, ABAA and BAAA and the electrostatic energy of each of these ordered arrangements may be calculated by standard procedures. As we do not know how to calculate correctly the energy of the disordered structure, we must deal with what is available; the energies of all the possible ordered arrangements of the cations.

The mineral columbite,  $\text{MnNb}_2\text{O}_6$ , offers a good example. In the orthorhombic unit cell are 12 cation sites occupied by 8 Nb and 4 Mn. The charges on the sites in the ordered structure (columbite) are either 5 or 2 and in the disordered structure (ixiolite) the average cation charge on all sites is 4. Barker and Graham<sup>6</sup> have calculated the electrostatic energy of columbite and ixiolite and find that the ordered arrangement is very much more stable than the disordered. This is difficult to reconcile