free energies, it is perhaps inevitable that φ cannot be regarded as strictly constant for interfacial tensions as well.

In some organic solids, notably polytetrafluoroethylene, stress relaxation may be relatively rapid on account of the known facility for molecular chain rotation and translation[7], a tendency which should be enhanced in the surface layers on account of diminished packing density. In such cases the distinction between interfacial tension and intrinsic surface energy will tend to disappear, although some dynamic effects concerning contact angles might well be attributed to the actual rate of stress relaxation in the interfacial zone.

The rectilinear relationship established empirically by Zisman et al. would, therefore, seem to be consistent with the view that wetting phenomena depend significantly on surface deformability as well as on intrinsic surface energy effects. Consequently, Young's equation does not describe the boundary conditions as well as Neumann's triangle, in spite of the prevailing view that the latter applies only to liquids. As a corollary, it may be conjectured that the surface layers of organic solids are partially disoriented and exhibit a degree of mobility more characteristic of a liquid or gel. Dynamic effects would, on the same view, depend on the actual magnitude of the relaxation time for molecular re-orientation at the interface[8].

G. R. LESTER

Imperial Chemical Industries, Ltd.,
    Dyestuffs Division,
        Hexagon House,
            Blackley, Manchester, 9.

[1] Girifalco, L. A., and Good, R. J., J. Phys. Chem., 61, 904 (1957).
[2] Young, T., Phil. Trans., 95, 65, 82 (1805).
[3] Fox, H. W., and Zisman, W. A., J. Coll. Sci., 5, 514 (1950).
[4] Lester, G. R., J. Coll. Sci., 16, 315 (1961).
[5] Gardon, J. L., J. Phys. Chem., 67, 1935 (1963).
[6] Neumann, F., Vorlesungen über die Theorie der Capillarität, 152 (Teubner, Leipzig, 1894).
[7] Bunn, C. W., and Howells, E. R., Nature, 174, 547 (1954).
[8] Rideal, E. K., and Tadayon, J., Proc. Roy. Soc., 225, 346 (1954).

Ca₈Si₅O₁₈ and the Nature of "γ-Dicalcium Silicate Hydrate"

HYDROTHERMAL treatment of mixtures of γ-Ca_2SiO_4 and quartz has yielded a new compound of probable composition $Ca_8Si_5O_{18}$, or $8CaO.5SiO_2$. This is formed, together with other products, over a wide range of conditions (bulk CaO : SiO_2 molar ratio 1·5–2·0, temperature 180°–600° C, pressure 10–200 bars, time 3–14 days). It has not yet been obtained in a pure form, but a preparation containing it with only small proportions of γ-Ca_2SiO_4 and wollastonite was obtained by treating a mixture of bulk CaO : SiO_2 ratio 1·75 for 14 days at 600° C and 200 bars.

The crystals were of micron size and anhedral. Selected-area electron diffraction showed them to be orthorhombic, with a, 11·54 Å; b, 5·09 Å; c, 28·86 Å. Systematic absences were found of $h0l$ reflexions with h odd, and of $0kl$ reflexions with l odd; the space group could therefore be $Pcam$ or $Pca2_1$. The principal X-ray powder spacings (in Å) were at 3·60 (ms), 3·05 (vs), 2·84 (s), 2·69 (s), 1·95 (ms), 1·895 (ms), and 1·806 (ms). The X-ray powder pattern was indexed and indicated cell parameters differing slightly from those obtained by electron diffraction: a, 11·45 Å; b, 5·09 Å; c, 28·70 Å. The ab-face of the unit cell is virtually identical in parameters with those of γ-Ca_2SiO_4 (ref. 1) and kilchoanite (a polymorph of $Ca_3Si_2O_7$) (refs. 2 and 3). Comparison of indexed X-ray powder patterns showed that the Fourier transforms of $Ca_8Si_5O_{18}$ and kilchoanite are closely similar. The infra-red absorption spectra of the two compounds are also very much alike.

These facts strongly suggest that the new compound has an interstratified structure formed by the regular alternation in the c-direction of layers of γ-Ca_2SiO_4 and kilchoanite. The unit cell of γ-Ca_2SiO_4 has c = 6·78 Å and atomic contents $4[Ca_2SiO_4]$ (ref. 1); that of kilchoanite has c = 21·95 Å and atomic contents $8[Ca_3Si_2O_7]$ (refs. 2 and 3). The unit cell of the interstratified compound would thus be expected to have c = 28·73 Å and atomic contents $4[Ca_8Si_5O_{18}]$. The predicted and observed cell parameters agree closely with each other, and the postulated chemical composition is compatible with the experimental evidence.

An apparent compound of composition $2CaO.SiO_2.0·26$–$1·00\ H_2O$ has been reported by various investigators as the product of hydrothermal treatment of β- or γ-Ca_2SiO_4 at 160°–300° C under pressures of saturated steam, and is generally known as "γ-dicalcium silicate hydrate" (ref. 4) or "$C_2SH(C)$" (ref. 5). The X-ray powder pattern, infra-red absorption spectrum, and thermal weight-loss curve of this material have been redetermined and are consistent with the view that it is a mixture consisting predominantly of calciochondrodite $(Ca_5(SiO_4)_2(OH)_2)$ (ref. 6) and $Ca_8Si_5O_{18}$ or a phase closely resembling it. Electron microscopy and selected-area electron diffraction (ref. 7) show that it also contains kilchoanite.

J. M. BENNETT
J. A. GARD
K. SPEAKMAN
H. F. W. TAYLOR

Department of Chemistry,
    University of Aberdeen.

[1] O'Daniel, H., and Tscheischwili, L., Z. Kristallogr., 104, 124 (1942). Agrell, S. O., and Gay, P., Nature, 189, 743 (1961).
[3] Roy, D. M., Gard, J. A., Nicol, A. W., and Taylor, H. F. W., Nature, 188, 1187 (1960).
[4] Taylor, H. F. W., The Chemistry of Cements, 1, 210 (Academic Press, London, 1964).
[5] Bogue, R. H., Mag. Concr. Res., 3, 87 (1953).
[6] Buckle, E. R., and Taylor, H. F. W., Amer. Mineralogist, 43, 818 (1958).
[7] Buckle, E. R., thesis, Univ. Aberdeen (1958).

Absorption Spectra of Methylene Blue in Benzene

DYES are generally investigated in aqueous media because of their insolubility in benzene and similar solvents. We have found[1] that many dyes, if extracted with benzene at a suitable pH, pass into the benzene medium, very often with a change of colour. This communication reports our preliminary results with methylene blue.

In Fig. 1, curves A and B are the absorption spectra of methylene blue in water and in a buffer of pH 11·2, respectively; it is evident that the shoulder of curve A at 610 mμ becomes quite prominent in the buffer. The shoulder has been ascribed by Rabinowitch and Epstein[2] to the dimer. The benzene extract of the dye solution in the aforementioned buffer is red in colour; curve C shows the absorption spectra in benzene. This red form of methylene blue was reported by Lewis[3] to be formed by the addition of hexane to an alcoholic solution of methylene blue. Lewis considered this to be a new form of dye. We recovered this red form of the dye as a solid (partly soluble) from the benzene extract by freeze-drying technique; the same could be dissolved in water and the absorption spectra are shown by curve D in Fig. 1. It would be seen that this red form has the peak exactly at the shoulder of the curves A and B. We conclude that the red form of methylene blue is not a new form of the dye as supposed by Lewis but is the dimer—its red colour in benzene being due to a solvent effect. The alternative idea that the red form is the carbinol base is discounted by the fact that the aqueous solution of the red form does not become blue on addition of acid. The shift in the position of the peak (curves C and D) is remarkably large. If the red form is dried strongly and dissolved in dry benzene, the position of the peak shifts somewhat towards longer wave-length, as is shown by the curve E. Evidently the effect of moisture on the absorption spectra of the red form of the dye is quite strong.