symmetry leads to replacement of the top and one side of a fourphase quadrilateral by the corresponding diagonal; the resulting triangle represents a three-phase equilibrium.

In addition to predicting, at least qualitatively, the existence of the multiple phase equilibria observed experimentally, our model also suggests the origin of the very low interfacial tensions between the separated microemulsion phases observed for certain systems<sup>2</sup>. In Fig. 2b the maximum difference  $\delta$ between the  $G^*$  curve and the double tangent is 0.0008, to be compared with a difference  $\delta' = 0.47$  between the reduced free energies for the corresponding homogeneous and phaseseparated mixtures in Fig. 2a. Although no quantitative calculations have yet been made, the implication is strong that a very thin layer of the bicontinuous phase can reduce the interfacial tension between a water-in-oil and an oil-in-water microemulsion by several orders of magnitude.



Fig. 3 The three- and four-phase regions at various values of  $\alpha^*$ .

Our aim has been to offer a minimal model of microemulsion phase equilibria, a model which leads to a purely entropic free energy function. In the absence of composition-dependent energy contributions, all phase equilibria should be independent of temperature, in apparent contradiction to experimental fact. It should be remembered, however, that the model assumes an ideal surfactant, one which exists only at the water/oil interface. The balance between hydrophilic and lipophilic interactions required for such optimal performance will in general be quite sensitive to temperature changes, particularly in the case of the surfactant-cosurfactant systems used in practice.

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Scriven, L. E. Nature 263, 123-125 (1976).
 Healy, R. N., Reed, R. L. & Stenmark, D. G. Soc. Petrol. Engng J. 16, 147-160 (1976).

(1976). <sup>3</sup> Meijering, J. L. Philips Res. Rep. **8**, 270–290 (1953). <sup>4</sup> Bernal, J. D. & Finney, J. L. Discuss. Faraday Soc.**43**, 62–69 (1967). <sup>5</sup> Finney, J. L. Proc. R. Soc. A **319**, 479–493 (1970).

## Toxic fluorinated compounds as by-products of certain BF<sub>3</sub>-catalysed industrial processes

We have embarked on a programme of toxicity tests on a range of industrial chemicals that are manufactured using boron trifluoride  $(BF_3)$  as a catalyst. Although this study is still in its early stages, we feel it opportune to draw attention to the fact that in some of the samples we have detected low concentrations of fluorinated compounds, some of which merit serious toxicological concern. The most notable example we have uncovered concerns some industrial chemicals that are manufactured from ethylene oxide using BF<sub>3</sub> as catalyst. On the basis of the results of toxicological studies of these products, we suspected fluoroacetate precursors as contaminants, and subsequent chemical analysis has confirmed the presence of low concentrations of 2-fluoroethanol and/or 2-(2-fluoroethoxy) ethanol. These two compounds are known to be very toxic to mice (LD<sub>50</sub> 10 and 15 mg kg<sup>-1</sup> respectively) and are regarded as fluoroacetate precursors<sup>1,2</sup>. The latter is the addition product of 2-fluoroethanol and ethylene oxide (equation 1), and 2-fluoroethanol is the formal addition product of fluoride ion to ethylene oxide (equation 2).

$$CH_{2}-CH_{2}+CH_{2}F.CH_{2}OH \rightarrow CH_{2}F.CH_{2}O.CH_{2}CH_{2}OH (1)$$

$$OH_{2}-CH_{2}+F \xrightarrow{-} CH_{2}F.CH_{2}OH (2)$$

This explanation of the genesis of the two fluoroacetate precursors points, not to BF<sub>3</sub> itself, but to fluoride ion as the source of the toxicants. That  $F^-$  is a common by-product of BF<sub>a</sub>-catalysed reactions is further supported by the identification of tetrafluoroborate ion  $(BF_4^-)$  as a contaminant of some of the other samples we have examined. For this chemical is the readily-formed product of interaction between F<sup>-</sup> and BF<sub>3</sub>. The origin of fluoride ion is unclear; it might derive by solvolysis of BF<sub>3</sub>-or of silicon tetrafluoride, SiF<sub>4</sub>, a known contaminant of commercial BF<sub>3</sub>.

Fuller details of these studies will be published elsewhere.

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<sup>1</sup> Buckle, F. J. & Saunder, B. C. J. Chem. Soc. 2774-2778 (1949).
<sup>2</sup> Pattison, F. L. M. Toxic Aliphatic Fluorine Compounds (Elsevier, Amsterdam, 1959).

## Aragonite in Permian Reefs

PRESERVATION of aragonite in fossils decreases the further we go back in the geologic record. In the Palaeozoic, aragonitic remains have been found only in clayeybituminous deposits which have largely inhibited diagenetic alterations of unstable mineral phases (for example, Buckhorn Asphalt and Kendrick Shale, both Upper Carboniferous of USA1, and Upper Oil Shale Group, Lower Carboniferous of Scotland<sup>2</sup>). Palaeontological information preserved in these facies is restricted, however, to those organic remains which lived in the equivalent basinal environments or were transported into them. Original mineralogy and microstructures of ancient reef organisms can generally only be deduced from analogies with equivalent younger counterparts. The oldest known reeforganisms with preserved aragonitic microstructures were