

In particular, there is a lack of reports of high magnesium tektites, the continental equivalent of the deep sea bottle green microtektites.

This lack of symmetry has led some people to question the identification of the Australasian microtektites. Other workers, on the other hand, believe that the absence of high magnesium tektites is more apparent than real, the problem being merely one of unrepresentative sampling. Moreover, and for a similar reason, the compositional range of even the normal tektites may not be as restricted as it has hitherto appeared. Glass, for example, has been carrying out detailed electron microprobe analyses of a single flanged australite (Australian tektite) and has found a remarkably wide range of composition within the one sample (*Earth Planet. Sci. Lett.*, **9**, 240; 1970). In particular, the silica content varies from 59 per cent to 85 per cent, which easily encompasses the 59 per cent to 76 per cent range of previously analysed normal microtektites. Furthermore, it compares with the previously reported range of 69 per cent to 79 per cent silica for twenty-three australite analyses. The point is that if a single australite can vary to this extent, similar analyses of other australites could easily result in a wider silica range which would encompass all microtektites whether normal or bottle green.

Thus, contrary to the impression given by previous limited data, Australasian tektites probably have a wide range of compositions. If this is the case, there is then no reason why the tektites and adjacent microtektites should not have had a common origin. Such a conclusion has always had strong circumstantial support but it has, until now, seemed to contradict the evidence from detailed analyses.

LIQUIDS

New Light on Solutions

from our Statistical Mechanics Correspondent

WHAT exactly happens when two liquids "mix" or when a solid is "soluble" in a liquid? This may be one of the oldest problems of physical chemistry but perhaps it is beginning to crack at last; some preliminary studies by Weres and Rice (*J. Chem. Phys.*, **52**, 4475; 1970) suggest that a theory of liquid solutions may now be possible. In solid solutions the atoms or molecules involved are usually about the same size, thus creating a balance between two opposing effects. Energetically like atoms usually prefer to be together. On the other hand, "mixed-up" configurations are far more numerous than "segregated" ones, so that thermal agitation tends to cause mixing of unlike molecules. In thermodynamic language, "there is a gain of entropy as a result of mixing" and, if the temperature is high enough, this can balance a loss of energy. If there were no difference in interaction energies between pairs of like and pairs of unlike molecules, "good" solubility could result (miscibility in all proportions), for the same reason that a mixture of red and blue grains of sand assumes a uniform colour when well stirred up.

This problem, of following qualitatively the balance between energy and entropy in a solid solution, has been studied, with various degrees of mathematical subtlety, since about 1930 a very important land-

mark being Onsager's famous *Physical Review* paper of 1944. Paradoxically therefore solid solutions are better understood than liquid solutions. One solid can be dispersed in another without, in many cases, any significant change of lattice structure, but this is probably never true of liquid solutions.

In a liquid, the interchange, by thermal agitation, of a pair of unlike molecules changes not only the energy and entropy, but also the immediate surroundings of both of these molecules. A liquid does not possess an actual lattice structure, but a "distribution function" can be defined that describes the average surroundings of a typical molecule. This function can be determined by X-ray and neutron scattering and, since about 1960, there have been theories for calculating it with reasonable accuracy. What still has to be allowed for, in discussing the solution process, is that the immediate surroundings of a large molecule may be very different from those of a small one.

Much theoretical work has been done on mixtures of non-attracting rigid spheres of different sizes, partly analytical, partly based on the use of large computers. Not surprisingly, theory predicts that, without interactions, there should be miscibility in all proportions. It should now be possible to put together a theory that balances the rather subtle geometric effects against the direct effects of intermolecular interaction and thermal agitation.

In some well known work in 1967, Barker and Henderson (*J. Chem. Phys.*, **47**, 2856 and 4714; 1967) showed that, if the properties of a (fictitious) assembly of hard non-interacting spheres are regarded as known, it is possible to devise a perturbation procedure that allows for the "softness" of real molecules and for the fact that, at large distances, they attract one another. This approach has been followed up by various other workers with very promising results. (It is obviously better to take the "rigid sphere fluid" as a starting point than to begin, as older theories did, with a solid or gas-like structure.) Many details remain to be worked out, but it is clear that this approach has come to stay. More recently, Weres and Rice have reported work on a perturbation treatment of liquid mixtures, starting from the now fairly well known properties of mixtures of non-attracting rigid spheres of two sizes. They studied the mixtures hydrogen-argon and methane-tetrafluoromethane which can be regarded fairly reasonably as molecules that behave as if they were spherical. After adjusting the interaction parameters to give the best possible agreement with the thermodynamic properties of the substances, they used a rather rough and ready procedure for estimating the interactions between unlike molecules and then attempted to calculate the thermodynamic properties of the mixtures. The agreement with experiment is reasonable for hydrogen-argon, less good for methane-tetrafluoromethane.

As always in this type of work, it is difficult to separate out the effects of the approximations used from the effects of our imperfect knowledge of the interactions. Nevertheless, the preliminary results of Weres and Rice suggest that recent work on mixtures of rigid spheres may be a satisfactory starting point for a theory of liquid solutions. As always, there are nagging doubts about the best way to set up a perturbation treatment, the rapidity of its convergence and the like, but these will not deter the enthusiast.