backward shift of the point of separation in pure water. It is possible to consider the reduction in friction factor of 'Polyox' solutions as a gradual motion of the point of separation back towards the trailing edge as *Re* increases. If this is so then the actual process of transition has been changed by the addition of polymer.

I thank Dr. A. M. Benis and Mr. D. Pike for their help and the Department of Chemical Engineering, University of Cambridge, for providing facilities to carry out the experiments.

D. A. WHITE

Department of Chemical Engineering,
University College,
London.

[1] Fabula, A. G., *Fourth Intern. Cong. Rheol.*, **3**, 455 (1964).
[2] Ruszczycky, M. A., *Nature*, **205**, 614 (1965).
[3] Uhlherr, P. H. T., *et al.*, *Chem. Eng. Sci.*, **20**, 997 (1965).
[4] Weiselberger, C., *Ergeb. Aerodyn. Ver. Göttingen*, **2**, 22 (1923).
[5] Prandl, L., and Tietjens, O. G., *Applied Hydro and Aeromechanics*, 98 (Dover, 1957).

Random Heap Structure of Liquids

BERNAL[1] has proposed a theory for the geometrical structure of liquids in which the arrangement of the atoms is totally irregular but nonetheless capable of being described by statistical means. In terms of a hard sphere model, Bernal postulates that liquids consist of close packed random heaps of spherical atoms, for which the volume packing density p_v is 0·637 (p_v is 0·741 for crystalline closest packing). On this basis, all liquids should have roughly similar structures characterized by this single value of p_v. This does not, however, rule out the likelihood of local structural differences between different liquids arising from the partial retention of crystalline structure, for the co-ordination type may change considerably yet be accompanied by only minor changes of packing parameter.

The random heap liquid structure has recently been used by Chadwick[2] in a hard sphere model of solidification leading to an explanation of the anisotropic nature of crystal growth. It is the purpose of this communication to show that the reliability of the random heap concept of liquid structure can be further tested by the use of the volume packing parameter. The hard sphere model results in a volume expansion on melting ΔV_f of about 14 per cent relative to the solid molar volume V_S. In practice, real materials (with the exception of the rare gas crystals) expand or contract by much smaller amounts, but the hard sphere model does not take into account the change in atomic radius resulting from the co-ordination change accompanying fusion. The observed values of $(\Delta V_f/V_S)$ are the result of the combined effect of a change in packing and a change in atomic radius. Noting that p_v is given by $4/3\ \pi r^3\ N/V_M$, where V_M is molar volume and N is Avogadro's number, the following equation may be obtained

$$\left(\frac{\Delta V_f}{V_S}\right) = \frac{p_v{}^S}{p_v{}^L}\left(\frac{r_L}{r_S}\right)^3 - 1$$

where r_L and r_S are the atomic radii of the liquid and solid, respectively, and $p_v{}^L$ and $p_v{}^S$ are the corresponding volume packing parameters. Since there is no unique value for the number of nearest neighbours in an irregular liquid, but instead a range within which the co-ordination number of any liquid atom can be found, it follows that there should not be a distinctive atomic size in the liquid. To a good approximation, however, r_L can be assumed to be given by the position of the main peak in the radial distribution function obtained by diffraction methods. For solids, of course, r_S is given by one half of the crystalline nearest neighbour distance.

Table 1 shows some values of (r_L/r_S) calculated from the foregoing equation for various crystal structures and for liquids assumed to consist of closed packed random heaps of hard spheres, for which $p_v{}^L = 0{\cdot}637$. Compared with the calculated (r_L/r_S) values in the table are experimental values of this ratio at the melting point, taking into account thermal expansion. (The data are taken from refs. 3–7.) The results suggest that the more densely packed metals and the face-centred cubic rare gas crystals (in which $p_v{}^S > 0{\cdot}50$) have similar structures when molten and that they are almost always consistent with random heap packing. (Hexagonally close packed magnesium and zinc seem to differ somewhat from this arrangement, but this may be caused—at least for zinc—by non-sphericity of the atoms.) On the other hand, the metalloids which have more open crystalline structures ($p_v{}^S < 0{\cdot}50$) show a less pronounced tendency toward the random heap liquid structure, deviating from it by rather larger amounts. It might be pointed out that the ratios shown in Table 1 are the result of taking cube roots, so that discrepancies appear smaller, but nevertheless the agreement between calculated and experimental (r_L/r_S) values remains striking, especially when it is considered that experimental values of r_L often differ by about 2 per cent.

Table 1. RELATIVE LIQUID/SOLID ATOMIC RADII BASED ON CLOSE PACKED RANDOM HEAP LIQUID STRUCTURES

Structure type	Material	$p_v{}^S$	(r_L/r_S) experimental	(r_L/r_S) calculated
	Densely packed metals, $p_v{}^S > 0{\cdot}50$			
Face centred cubic *A*1	Pb	0·741	0·96	0·96
	Ag	,,	0·97	0·96
	Au	,,	0·97	0·97
	Al	,,	1·01	0·97
Body centred cubic *A*2	Li	0·680	1·02	0·99
	Na	,,	1·02	0·99
	K	,,	1·00	0·99
	Rb	,,	0·99	0·99
	Cs	,,	1·01	0·99
	Tl	,,	0·99	0·99
Hexagonal close packed *A*3	Mg	0·730	1·03	0·97
	Zn	0·653	1·08	1·01
	Cd	0·643	1·02	1·01
Tetragonal *A*5	Sn	0·535	1·07	1·07
Tetragonal *A*6	In	0·688	0·97	0·98
Rhombohedral *A*10	Hg	0·607	1·03	1·03
	Rare gas crystals			
Face centred cubic *A*1	Ne	0·741	0·96	0·98
	Ar	,,	0·98	0·99
	Kr	,,	0·99	0·97
	Xe	,,	1·00	1·00
	Loosely packed metalloids, $p_v{}^S < 0{\cdot}50$			
Diamond cubic *A*4	Ge	0·340	1·10	1·21
Rhombohedral *A*7	Bi	0·448	1·07	1·11
	Sb	0·425	1·07	1·12
Orthorhombic *A*11	Ga	0·390	1·14	1·16

I thank the National Research Council of Canada for a post-doctoral research fellowship, and Dr. G. A. Chadwick for his many valuable suggestions.

W. A. MILLER

Department of Metallurgy,
University of Cambridge.

[1] Bernal, J. D., in *Liquids: Structure, Properties, Solid Interactions*, edit. by Hughel, T. J., 25 (Elsevier, Amsterdam, London, New York, 1965).
[2] Chadwick, G. A., *J. Phys. Chem. Solids* (in the press).
[3] Taylor, A., *X-Ray Metallography* (John Wiley, New York and London, 1961).
[4] Wilson, J. R., *Met. Rev.*, **10**, 381 (1965).
[5] Furukawa, K., *Rept. Prog. Phys.*, **25**, 395 (1962).
[6] Borelius, G., *Solid State Physics*, **15**, 1 (1963).
[7] Henshaw, D. G., *Phys. Rev.*, **111**, 1470 (1958).

CHEMISTRY

Hydride Transfer Reactions catalysed by Metal Complexes

IN the course of an investigation of the catalytic action of certain metal complexes in hydride transfer reactions it was observed that rhodium chloride catalysed the dehydrogenation of isopropanol to acetone. During the reaction rhodium metal was precipitated, and it was found that the rate of dehydrogenation decreased as rhodium was removed from solution. For example, when a 100 ml. solution of isopropanol containing 0·0076 M rhodium trichloride, 0·094 M lithium chloride and 0·29 M