LIQUID METALS

A CONFERENCE was held at the Fulmer Research Institute, Stoke Poges, to bring together as many as possible of the workers concerned with the experimental study of liquid metals. The meeting was convened with the help and encouragement of Dr. B. R. T. Frost, of the Metallurgy Division of the Atomic Energy Research Establishment, Harwell. Prof. J. D. Bernal (Birkbeck College, University of London) acted as chairman.

Dr. J. E. Enderby (University of Sheffield) directed attention to the considerable variation found in the absolute value of the resistivity (ρ) (at constant volume) and the way in which it varies with temperature. The resistivities of sodium and potassium are strictly proportional to the absolute temperature; in contrast, divalent metals, zinc, cadmium and mercury, have a negative temperature coefficient. Values of the resistivity ratio ($\rho_{\text{liquid}}/\rho_{\text{solid}}$) vary between 1.45 and 2.2; a trend exists through the alkali metals and the noble metals which is related to the energy-gap across the Brillouin zone boundary. The change in thermoelectric power across the melting-point has the value 0 for sodium, silver and gold, but for copper it is as high as 9.5. Hall coefficient measurements give the free electron value. Thus for metals such as zinc and cadmium the coefficient changes sign and becomes negative on melting.

Mr. B. W. Mott (Harwell) dealt with a modification of the Hildebrand rule which can be used to predict immiscibility in alloy systems. A parameter is calculated, the Mott number, which depends on the atomic volume, heat of evaporation and electronegativity of each of the components, together with the melting-point of the more refractory metal. There will be immiscibility if the Mott number is lower than the smallest Pauling valency. The main difficulty involves the selection of electronegativity values, those given by the Gordy relationship predict immiscibility in 84 per cent of the 886 systems examined.

Simple X-ray diffraction patterns, obtained from pure molten metals such as sodium and copper, can be contrasted with those from metals where structure can be shown to exist, gallium, bismuth and tin. In the case of liquid tin Mr. B. R. Orton (Fulmer Research Institute, now at Brunel College of Advanced Technology) was able to show that, by careful calculation of the radial distribution function, two atomic species are present in the melt. One can be identified with covalent grey tin, the other forms the random matrix of metallic white tin. For other metals which occupy the *B* groups of the periodic table it is possible to show that the participation of the covalent bond increases with valency. Diffraction patterns from liquid alloys also show structure. In the gold-tin alloy system a dominant structure is found which corresponds in composition to the solid-state electron compound, Au_3Sn . Other alloy systems show structure (copper-indium, copper-tin, silver-indium, gold-gallium and gold-indium). At the same valency electron concentration, different alloys of the above group show similar diffraction patterns.

Dr. H. N. V. Temperley (Atomic Weapons Research Establishment, Aldermaston) proposed that previous machine calculations, based on the rigid sphere model of a liquid, should help in the understanding of solidification. There is, however, very poor agreement with approximate theories in the high-density region. In addition to more detailed calculations, a new field is opened in Bernal's statistical geometry. The two-dimensional case is being investigated first. Two models of the lattice type are considered, rigid square and rigid rod. The first has the restriction that the presence of a molecule at one point on a square lattice prevents the occupation of the four

neighbouring points. This model shows a transition between a completely disordered arrangement at low density and an alternating structure at high density. Transitions from one to the other are found to be first-order transitions in the Ehrenfest sense. This is in qualitative agreement with the results for rigid spheres. In the second model the molecules are identified with pairs of neighbouring points, no lattice point being occupied more than once. This model is more satisfactory for mathematical study, though only very general results are obtained.

Dr. P. A. Egelstaff (Harwell) described how cold neutrons can be utilized in the study of diffusion in liquids. Most of the existing theories consider the diffusion process to be either gas-like or solid-like. If these models are applied to the viscosity and diffusion data on liquids it is concluded that liquid diffusion is unlike either of the two starting points. A new model is formulated that involves the co-operative action of a number of atoms, termed 'globules'. Predictions are made, using this model, which are confirmed by experimental results, thus giving direct evidence of co-operative units in liquid metals.

Another model was proposed, by Dr. J. Wilson (University of Birmingham), in which the liquid is visualized as consisting of atomic clusters having a definite structure in a matrix of randomly arranged atoms. A state of dynamic equilibrium exists between the clusters and the matrix. The structure of the clusters need not be the same as that of the corresponding solid. The lifetime of the clusters, composed of 50–150 atoms, may be one or two orders greater than the relaxation time of the liquid. This model provides an explanation of the minimum value found in the plot of viscosity against composition for certain eutectic alloys. The minimum represents a transition point between the liquid alloy being dominated by one or other of the pure components. Other published data confirm this model.

Describing the inadequate state of the theories of thermodynamics when applied to the explanation of the nature of the bonds in alloy formation, Dr. S. Ll. Leach (Royal School of Mines, University of London) suggested an alternative procedure. The thermodynamic properties must be considered with other physical properties (resistivity and X-ray diffraction measurements) to give a complete picture. He quoted, as an example, the gold-tin alloy system, where all this information is available. From the X-ray measurements it is deduced that there are two types of bond, the short-range covalent and long-range metallic bond. The published resistivity measurements support this view. A maximum, which is independent of temperature, is found at the composition Au_3Sn . It seems possible that as the temperature of the liquid is raised the covalent bonds break down and the electrons released just compensate for the increase in thermal scattering. The success of this approach has led the Royal School of Mines to embark on a programme of experimental measurements of a number of physical properties on one or two selected alloy systems.

The chairman, Prof. J. D. Bernal, concluded the meeting with some general comments on the nature of pure liquids and alloys. The transition from solid to liquid could, he said, be associated with higher vibration-levels, changes in geometrical configuration, greater disorder, lower co-ordination number and lower mean lattice energy. For ideal liquids, machine calculations have emphasized the importance of the short-range forces. If these forces only are taken into account then a discontinuity is found which corresponds to the solid to liquid transition. To understand the liquid to gas transition the

behaviour of argon above the critical point is important. There is no single fluid phase but two distinct states of matter even though there is no visible discontinuity.

Commenting on the models of Dr. Egelstaff and Dr. Wilson, Prof. Bernal suggested that the presence of globules could be detected by the use of small-angle scatter and an estimate of their size obtained from viscosity measurements.

Turning next to alloys, Prof. Bernal put forward the idea that they could be considered as emulsions and cited as evidence the presence of the γ -phase in alloys of copper, silver or gold with zinc. In this phase the atoms are distributed at random over the lattice sites. However, the electron compound found in the gold-tin alloy system could be the cause of the structure observed in the X-ray diffraction patterns.

B. R. ORTON

RADIOACTIVE CHEMICALS, LABELLED COMPOUNDS AND RADIATION SOURCES

FOR most purposes, particularly in engineering and radiotherapy, where the radiological properties of radioisotopes are of paramount importance, it is generally sufficient to refer to the tabulated physical data given in Part 1 of *The Radiochemical Manual* for a suitable choice of radioactive material. However, in the case of radioactive tracers for use in the biological sciences, chemical technology and related fields, the purity, chemical stability and the characteristic behaviour of the isotopes as radioactive chemicals are often the decisive factors, and for these Part 2 of the *Manual**, which has recently been published and which deals with the chemical aspects of radioactive materials, must be consulted.

The range of radioactive chemicals is very extensive, and Part 2 has therefore been limited to a number of articles on selected topics likely to be useful to users of radioactive tracers. The examples referred to are drawn largely from the practical experience of the scientific staff at the Radiochemical Centre at Amersham. The contents of Part 2 consist of three sections, dealing with the sources of radioactive chemicals, some characteristic features of the chemicals, and notes on labelled compounds of the elements carbon, hydrogen, sulphur, phosphorus, iodine and chlorine.

The first section contains four chapters in which the distinctive features which affect the manufacture of radioactive reagents are outlined. Radiological protection and remote handling frequently limit the types of chemical manipulation which can be carried out. The half-life of the isotope is the important factor in the organization of supply and distribution, and the chemical scale of manufacture which rarely exceeds one gram is a unique feature. The distinction between primary isotopes and labelled compounds is clearly drawn and the various methods of preparation are explained. Isotopic labelling and its wider implications, the synthesis of labelled compounds by chemical and biological methods and some of the unresolved problems such as the isotopic labelling of natural products by biosynthesis, are also discussed.

Chapters 5-7, which form the second section, are concerned with the concepts of purity and its determination, instability, and the behaviour of minute quantities and dilute solutions of radioactive chemicals. The final six chapters in the third section refer individually to compounds of each of the six elements which are most commonly concerned in tracer experiments. Carbon-14, which emits only β -particles, is produced by means of a

reactor in adequate quantities and at high specific activity, and, since it has a half-life of 5,760 years, it is a most favourable tracer isotope. It has been used for the intensive study of biochemical processes and has now virtually displaced the stable isotope carbon-13 and the short-lived (20 min) radioactive isotope carbon-11. Tritium-labelled compounds are now second in importance to carbon-14 compounds in biochemical tracer work, but tritium is not used as a hydrogen tracer but as an accessory tracer for a carbon atom or a molecule or a molecular fragment. Tritium is available in quantity and high specific activity (up to 29 c./m.amp) and its half-life of 12.3 years is conveniently long.

Sulphur-35 is the only practicable label for sulphur atoms. Its half-life is 87.2 days, and although it can be produced by direct neutron irradiation, it is better extracted as sulphate at high specific activity from neutron-irradiated potassium chloride. The main groups of chemical in which sulphur-35-labelled compounds are of interest are listed in the *Manual*. Phosphorus-32 is relatively easy to prepare. Its half-life is 14.2 days and its main applications are in inorganic fertilizers, nerve gases, systemic insecticides, and plasticizers. Iodine-131 is in abundant supply from irradiated tellurium or from fission products, but its short half-life prevents stock-holding of iodine-labelled compounds. Other isotopes of iodine, iodine-132, iodine-125 and iodine-124, are also available. Chlorine-36 has a long half-life of 3.03×10^5 years and is a pure β -emitter of medium energy. Its production is expensive and its specific activity is low, less than 4 mc./m.amp. Chlorine, however, is an important industrial chemical and therefore chlorine-36 has valuable applications. It is also in many ways an ideal radio-isotope for use in the teaching of practical chemistry.

Part 2 of the *Manual* concludes with thirteen tables of synthetic routes to labelled compounds, a glossary of terms used, and numerous references to published work relating to the topics discussed and the tables. For details of the products, radioactive chemicals and radioactive sources, and services provided by the Radiochemical Centre the reader is referred to the catalogue, *Radioactive Products*†, available on request from the Centre.

S. WEINTROUB

* *The Radiochemical Manual*, Part 2: *Radioactive Chemicals*. Pp. v + 78. (Amersham: The Radiochemical Centre, 1963.) 25s.

† *Radioactive Products: Radioisotopes, Labelled Compounds, and Radiation Sources*. Pp. 119. (Amersham: The Radiochemical Centre, 1962.)

RESEARCH INTO TECHNICAL EDUCATION

THE report of a working party, with Prof. A. V. Judges as chairman, set up at the second session of a conference on June 6, 1961, presided over by Dr. Dunsheath, and attended by representatives of the University of London, the Regional Advisory Council for Technological Education (London and Home Counties), local authorities, technical colleges and research institutions, has now been published under the title *Research into*

*Technical Education**. The working party was charged, *inter alia*, with considering priorities in research in this field and, apart from the specific proposals for research which are detailed, the report gives in its introduction an admirable survey of the present position and of the

* *Research into Technical Education: Report of a Working Party*. Pp. 34. (London: The Regional Advisory Council for Technological Education, London and Home Counties, 1963.) 5s.