

CO-ORDINATION CHEMISTRY

THE eighth international conference on "Co-ordination Chemistry" brought together some 750 research workers in Vienna during September 7-16 and gave rise to two cognate symposia, one in Czechoslovakia and the other in Hungary.

The symposium in Hungary, held at Tihany, Lake Balaton, during September 14-17, under the auspices of the Hungarian Chemical Society, with Prof. G. Schay as president and Dr. M. T. Beck as secretary, was attended by about 60 Hungarian chemists and some 100 visitors from countries as distant as the United States and Japan. The papers were preprinted in full in two octavo volumes totalling 886 pages, and authors were allowed 15 min to introduce their papers followed by 10 min discussion. The papers were drawn equally from countries east and west of the 'Iron Curtain', and the conference afforded an excellent opportunity for Western chemists to meet their counterparts from the East. The two volumes make very interesting reading, containing many authoritative reviews with new work from well-known authors. They will be published together with the discussion in the near future, and are warmly recommended to those who did not have the good fortune to attend the conference.

Tihany is a beautifully situated holiday resort on Lake Balaton and, appropriately to this wine-producing area, the lectures and discussions took place in the 'Bar' of the Tihany Motel. Participants from abroad were accommodated at the Tihany Hotel, about 100 yards away. Forty papers were presented and raised much interesting discussion, so that in many cases the discussion time was much too short. Briefly, the papers touched on the following points, and only the authors who presented papers are mentioned.

Outer sphere association of complex cations and simple anions has been examined by charge transfer spectra (C. K. Jørgensen, Switzerland) and optical rotatory dispersion (S. Kirschner, United States). Perhaps the most remarkable fact is the high degree of association which can occur. R. Larsson (Sweden) reported successive stability constants for up to four thiosulphate ions with $d\text{-}[\text{Coen}_3]^{3+}$ forming a super anion of charge 5- and requiring, for the later stages of its formation, the association of negative ions in aqueous solution of ionic strength 2.

The four papers on homogeneous hydrogenation (J. Halpern, United States; V. A. Tuloupov, U.S.S.R.; J. C. Bailar, jun., United States; and L. Simándi, Hungary) contained much new material leading to a lively discussion and firmly pointing the way to selective and specific catalysts. This was followed by papers on ligand interaction with 5f orbitals (B. Jezowska-Trzebiatowska, Poland) and some acetylacetonate complexes of the uranyl ion (J. Szóke, Hungary).

A major part of the programme concerned the chemistry of aqueous solutions of complex ions. L. G. Sillén (Sweden) made an earnest plea for care in interpreting stability constant measurements and emphasized the value of a computer for checking data and calculating constants. This was followed by papers concerned with the quantitative aspects of the formation of polynuclear complexes in aqueous solution. P. Szarvas (Hungary) discussed the equilibria between isopolytungstic acids and tungstate-carboxylic acid complexes, A. E. Martell (United States) the formation and possible structures of polynuclear species derived from polyfunctional organic ligands and tri- and tetra-positive ions, and A. Gergely (Hungary) the equilibria between neodymium(III) ion and d -glycosaminic acid.

J. Bjerrum (Denmark) reviewed and correlated the great variety of different complex formation curves obtained from ligands with Cu(I), Ag(I), Au(I) and Hg(II),

including new data on organic phosphines and arsines as ligands. This was followed by a paper on the formation of azido complexes in non-aqueous solvents by V. Gutmann (Austria), and a comprehensive account of the formation of mixed dimethylglyoxime (DMG) complexes of general type $M(\text{DMG})_2X_n$ ($M = \text{Mn(II), Fe(II), Co(II), Co(III), Cu(II)}$ and Pd(II) ; $X = \text{halide ion, OH,}$ and other ligands; $n = 1$ or 2) (K. Burger, Hungary). Only nickel failed to form such complexes, and this was advanced as the main reason for relative insolubility of $\text{Ni}(\text{DMG})_2$ in water.

Solvent extraction of metal ions through complex-formation with organic ligands and the enormous enhancement of the extraction by some ligand mixtures were described in papers by H. Irving (England), D. Dyrssen (Sweden), and L. Bakos (Hungary). W. K. Wilmarth (United States) discussed the base catalysed reduction of μ -peroxo bridged complexes of cobalt, and D. Konrad (Czechoslovakia) the extraction of halogen from halogenated hydrocarbons by complexes of transition metals in low valent states. The retardation of hydroformylation and hydrogenation of olefines on a cobalt catalyst was attributed by L. Markó (Hungary) to the formation of cobalt sulphide by means of cobalt carbonyl derivations such as $\text{Co}_3(\text{CO})_9(\text{S})$ and $\text{Co}_3(\text{CO})_9(\text{S})(\text{SR})$, the sulphide being stable under carbonylation conditions.

Polymeric and polynuclear complexes formed the subject of a number of papers. The formation of oxygen bridged complex fluorides by the thermal condensation of hydroxofluoro complexes of arsenic and antimony was discussed by L. Kolditz (East Germany), and thermal degradation of the infinitely bridged complexes of methylpiperazines with cobalt halides to the binuclear $[\text{diamine}_2\text{Co}_2X_4]$ by E. Körös (Hungary). The structures and thermal decomposition of polymeric alkoxy bridged complexes were the subject of papers by D. C. Bradley (Canada), F. Majdik (Hungary) and Gy. Pfeifer (Hungary). Gy. Bor (Hungary) gave a detailed account of the application of infra-red spectroscopy to determining the structure of polynuclear metal carbonyls, and showed that the "method of local symmetry" is invalid. Infra-red and Raman spectral investigations were also carried out to determine the type of bonding in mixed halide-cyanide complexes of gold(III), for example $[\text{AuCl}_2(\text{CN})_2]^-$ (L. H. Jones, United States).

Polynuclear complexes containing metal-metal bonds were reviewed and classified by R. S. Nyholm (England), who also described a number of new compounds in which a covalent metal-metal bond was an essential link, for example $[\text{CH}_3\text{C}(\text{CH}_2\text{AsMe}_2)_3\text{Cu.Mn}(\text{CO})_5]$.

E. Thilo (East Germany) attributed the catalytic effect of metal ions on the hydrolysis of polyphosphates and pyrosulphate to the chelation of the cations by the polyanion. A very thorough tracer investigation of the alkaline hydrolysis of pentamminecobalt(III) carboxylates by H. Taube (United States) showed that it proceeded by two paths, at low temperatures and high $[\text{OH}^-]$ by C-O bond breaking and at high temperatures (90°) and low $[\text{OH}^-]$ (0.01 M) by breaking of the Co-O bond. The rate-determining step in strong acid hydrolysis of $\text{cis-}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$ involved the protonation of the complex with splitting away of HC_2O_4^- (H. L. Schläfer, West Germany).

Equilibrium studies of the stabilities of mixed complexes in aqueous solution were given by I. Leden (Sweden) and by E. J. Marcus (Israel). It is often found that the mixed complexes are more stable than would be expected on the basis of the stabilities of the corresponding binary complexes, for example, HgClI exists in greater concentration than would be expected statistically from the

stability constants of HgCl_2 and HgI_2 . Marcus generalized that the more unlike the ligands the more stabilized the mixed complex provided the two ligands form complexes of the same bonding type, and calculated the stabilization in terms of a polarized ion model.

The remaining six papers were concerned mainly with the effect of ligands on electron transfer reactions and the

redox properties of complexes (C. H. Brubaker, jun., United States; G. M. Nord-Waand, Denmark; W. Langenbeck, East Germany; and L. Kiss, Hungary), concluding with a systematic review of the mechanism of catalysed redox reactions including catalysis by so-called 'inert' complexes (M. T. Beck, Hungary).

J. CHATT

A SIMPLE MASS SPECTROMETER FOR THE ANALYSIS OF ARGON AT ULTRA-HIGH VACUUM

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THE most modern methods of determining the ages of rock formations are based on radioactivity^{1,2}, perhaps the most widely used technique so far being that utilizing the decay of potassium-40 to argon-40. Potassium-40 is a long-lived rare isotope of potassium (0.0119 per cent atomic) and by virtue of a branching decay produces both argon-40 and calcium-40. A potassium-argon age measurement on a mineral involves two steps: (a) determination of the potassium concentration by acid digestion of the mineral followed by flame-photometry; (b) evaluation of the argon concentration by fusion of the mineral in vacuum followed by mass spectrometric, isotope dilution measurements on the evolved argon. While many laboratories have the facilities for potassium analysis, equally many are deterred from setting up methods of argon analysis because of the considerable expense usually thought to be involved in the acquisition of a suitable mass spectrometer. However, we have recently been experimenting with a simple, inexpensive mass spectrometer, the MS10, bought from Associated Electrical Industries, Ltd., and wish to report here its successful application to potassium-argon dating.

The instrument uses a 2-in. radius of curvature with 180° deflexion. A magnetic field of 1,830 gauss is produced by the small permanent magnet, and electrostatic scanning of the various ion beams is brought about by a motor-driven potentiometer in the source controls which causes the appropriate variations in accelerating voltage. When argon-40 is focused on to the collector slit the accelerating voltage is about 100 V. Ions are generated by the usual electron impact method of ionization³, the ionizing electrons being emitted from a heated rhenium filament prior to being accelerated by falling through a potential difference of 70 V. Stable ion beams are produced with the trap current regulated at 50 μamp and these are detected with a d.c. amplifier having a $10^{11} \Omega$ input resistor. The output is fed to a Honeywell-Brown potentiometric pen recorder, where the noise-level is less than an equivalent ion current of 2×10^{-15} amp.

Use of the static method⁴ of analysis in mass spectrometry produces a great increase in sensitivity over the more usual dynamic mode. In the former technique a small fraction of gas from the inlet system is admitted to the tube, where it is then completely isolated and analysed. This requires that before such an analysis may be carried out the vacuum inside the mass spectrometer must be sufficient to ensure that isolation of the tube from the pumping system during a static analysis does not cause a significant rise in pressure. To satisfy such a requirement we have set up the MS10 so that it may be baked out inside an oven while being pumped out. The instrument is designed for regular baking at temperatures up to 400° C, but we have not found it necessary to exceed 200° C. With overnight baking little difficulty has been experienced in producing pressures of about 5×10^{-10} mm

mercury, and these have been maintained, without further baking, over periods of several months. The pumping system uses a silicone oil, Dow Corning '705', in a metal diffusion pump—the latter being separated from the mass spectrometer tube by a liquid air trap, and being backed by a simple rotary pump. No difficulty has been experienced in reducing the background at the critical mass 36 to zero. At pressures of the order 5×10^{-10} mm mercury, the only significant peak occurs at mass 28 and is presumed to be due to nitrogen and carbon monoxide.

A very simple inlet system has been used and may be seen in Fig. 1. It is a simple matter to evacuate the inlet side so that any background contributions in the inlet at masses 36 and 38 are not detectable by the mass spectrometer and any at mass 40 is only just seen on the most sensitive range. Samples left overnight in the inlet system show no variation in 36/38 and 40/38 ratios with time.

It has frequently been reported by mass spectrometry workers that in static analysis the gases being analysed during a particular measurement are contaminated by a previous sample. Reynolds⁴ has suggested that during an analysis ions are driven into the walls of the mass spectrometer tube. The composition of the embedded gases

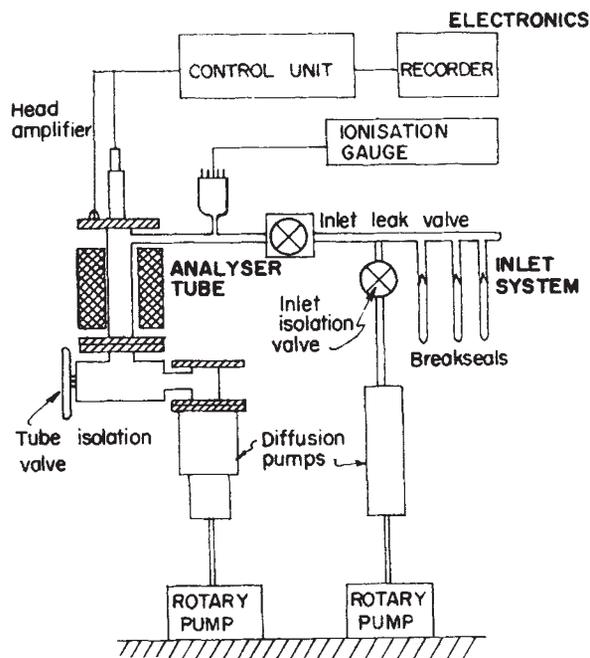


Fig. 1. Schematic diagram of experimental arrangement for static analysis of small volumes of argon on MS10 mass spectrometer