Coordination Chemistry in Fused-Salt Solutions

Spectrophotometric work on structural determinations with fused-salt solutions is reviewed (1). The constraints placed on the method, as well as interpretation of the spectra, are discussed, with parallels drawn to aqueous spectrophotometric curves of the same materials.

In attempts to overcome the limitations of water as a solvent and to study new chemical reactions, many "nonaqueous" solvent systems have been investigated, among which fused salts constitute a particularly extensive and unique class of inorganic solvents. The study of chemical reactions in fused salts is of scientific interest, primarily because of the possibilities offered by these unusual high-temperature solvents for exploration of new chemical phenomena.

For study of the chemistry of fused salts, new methods and techniques have been developed, and older ones modified, to cope with the special problems that arise with these materials. Now one can study them by a startling variety of techniques including electrochemical-potential measurements, polarography, chronopotentiometry, chromatography, electromigration, solvent extraction, nuclear magnetic resonance, and electron spin resonance.

Since it is clearly impossible to cover the tremendous amount of research on fused salts during the last decade, this review is limited to results by one technique—absorption spectrophotometry. Absorption spectra are especially useful for study of the solution chemistry of transition-metal ions; their unique features enable one to characterize the oxidation states of the ions, determine their concentrations, and establish the identities and stabilities of complex ionic species. By means of spectral changes, one can follow the courses of chemical reactions and study their kinetics and mechanisms.

Although spectral measurements have long been used for aqueous solutions, specialized techniques for making quantitative spectral measurements of fused-salt solutions are only recently developed. One problem to be solved, for measurement of absorption spectra of fused salts at high temperatures, entailed the elimination of black-body radiation, emitted by the sample, sample container, and furnace, from the detection system. The solution is use of a source of chopped radiation, coupled with phase-sensitive amplification, in the following sequence of components: light source → chopper → sample and furnace → monochromator → detector → a-c amplifier → recorder.

Use of instrumentation having these design features has made possible measurement of absorption spectra at high temperatures (about 1,000°C) with the same accuracy as from conventional aqueous solutions at room temperature.

Reference:
1. D. M. Gruen, "Coordination chemistry in fused salt solutions" (Argonne National Laboratory, June 1967).

Notes:
1. Metals-producers and coordination chemists may be interested.
2. Inquiries concerning this innovation may be directed to:
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Patent status:
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