STANDARD REFERENCE ELECTRODE FOR MOLTEN SALTS

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ABSTRACT

The definition of the Ag(I)/Ag reference electrode as a standard reference electrode for fused salt media is discussed. The required definitions are three: the definition of the fused salt solvent system in terms of nominal composition, nominal temperature, and nominal composition; the definition of a solute concentration in terms of mole ratios; and the definition of the standard state of Ag(I) as that which prevails in sufficiently (ideally, infinitely) dilute solutions. The experimental construction of such an electrode is discussed.

Introduction

Molten salts constitute a diverse class of solvent systems in which various reference electrodes have been proposed and used. These reference electrodes have been of diverse types, but in virtually all cases the potential of the Ag(I)/Ag(0) couple has been carefully measured against the reference electrode used. It is proposed that the standard reference electrode in molten salts be based upon the Ag(I)/Ag(0) couple. In order to do so the conditions of measurement and of the standard itself must be unambiguously specified both in terms of the molten salt solvent system and in terms of the state of components of the reference electrode couple.

Definition of a Solvent System

A solvent system, whether for fused salt media or not, is defined as a uniform single-phase liquid chemical system whose nominal temperature, nominal pressure, and nominal composition can be unambiguously expressed in SI units. The nominal temperature is best expressed in kelvins (K), the nominal pressure in pascals (Pa), and the nominal composition in terms of amount of substance for
which the unit is the mole. Specification of several fused salt solvent systems has been done in detail elsewhere (1).

The nominal composition of a fused salt solvent system is its most fundamental defining parameter. The solvent system can be defined as consisting of a single compound, such as NaCl or NaAlCl₄, but it is more often convenient to specify a fixed mole ratio of two or more compounds, such as equimolar NaCl-KCl or NaOH-KOH, because the melting point of the mixture is well below that of either of the pure compounds and the range of temperatures accessible to measurement is significantly increased. Alternative specifications include mass ratio, which requires knowledge of the molecular weights of the constituent salts, or the eutectic composition, in which case the mole ratio of the eutectic composition must be accurately known. It is fortunate that preparation of a molten salt solvent system by measurement of component volumes is sufficiently inconvenient as to be unknown and so specification of composition as a volume ratio is not used; the complication that the volume of a mixture is not equal to the sum of the separate volumes of its components is thereby avoided.

The nominal temperature of a solvent system is defined empirically, but generally a consensus exists (1); in any event, measurements are usually made over a range of temperatures above and below the nominal temperature. The nominal temperature is selected as a convenient temperature above, usually well above, the melting point of the defined composition and below the temperature at which undesirable reactions of the solvent (decomposition, vaporization) or of the container materials (softening of glass, corrosion) become significant within the few hours normally required for completion of a series of experiments in a molten salt system.

The nominal pressure is almost invariably taken as one standard atmosphere (101.324 kPa) of an inert gas, i.e., a total pressure of exactly one atmosphere made up of the vapor pressure of the molten salt (very low) plus a pressure of an inert gas. For certain molten salts, such as carbonates, the gas cannot be inert and must be specified in order to prevent solvent decomposition; the total pressure remains one atmosphere.

The compilations of Janz and co-workers on density (2) and eutectic composition (3) are extremely valuable in
Definition and characterization of molten salt solvent systems. Specific preparation procedures are compiled by Plambeck (1).

Definition of a Solute

A solute in a solvent system is any component present other than those of the nominal composition. The amount of solute is specified in terms of its concentration, which must be interpretable as a ratio between amount of solute (in mol) and amount of solvent system (in mol). This ratio is itself the concentration on the mole fraction scale, which is the most fundamental measure of concentration but is also the concentration scale on which unity is the farthest removed from actual experimental conditions of measurement in dilute solutions. The use of the molality scale (mol solute/kg solvent system) and molarity scale (mol solute/dm³ solution) is common in molten salt studies since unit concentration on these scales is experimentally accessible. Conversion of molality data to mole fraction requires only knowledge of molecular weights, but conversion of molarity data requires knowledge of the solvent system density (2) as well. The density of the solvent system can be taken as equal to the density of the solution, as is the almost universal practice, only for dilute solutions without introduction of serious error. The molarity scale is therefore suitable only for measurements in dilute solutions. In practice, measurements below a mole fraction of 0.01 will have a negligible error from this source.

Definition of Standard States for Reference Couples

Any electrochemical couple which can produce a reversible electromotive force consists of at least two species which differ in charge. In molten salt solvent systems, either one or both of these species are solutes and for the simplest couples such as Fe(III)/Fe(II) or Ag(I)/Ag(0) these solutes are ions. The standard states of all species involved in an electrochemical couple are the states which define the conditions under which the actual potential of the couple is taken as its standard potential against a reference electrode or, in the case of a reference electrode, the conditions under which its actual potential is taken to be exactly zero so that the entire measured potential difference is ascribed to the
electrode whose potential is being measured against that of the reference electrode.

The standard state is necessarily taken as that of the nominal temperature, pressure, and composition of the molten salt solvent system. For a pure element or compound such as silver metal no more is required; if the nominal temperature is above 961°C the standard state is liquid silver and below that it is the solid metal. Likewise, for a material which is a constituent of the solvent system itself or is linked to a constituent by an equilibrium, no more is required because the activity of such a species is fixed by the composition of the solvent system. Couples for which both or all of the species involved are thus of fixed activity are often used as reference electrodes in molten salts. Examples include the Cl2(g, 1 atm), C/Cl− couple in equimolar NaCl–KCl (4) and the Al(III)/Al(0) couple in melts containing AlCl3 as a constituent. Such reference couples are convenient, or even possible, in a comparatively small number of melts and differ considerably from one melt composition to another. Although the standard states are indeed well defined and the potentials are often well poised, such couples cannot form the basis of a universal or widely-applicable standard reference electrode for molten salt solvents.

As a consequence, the standard state of a solute such as Ag(I) must be taken as the state of Ag(I) in which the Ag(I) has a negligible effect upon the composition of the molten salt solvent system, which is to say in a sufficiently dilute solution that the behavior with concentration is, within experimental error, that of the infinitely dilute solution. For the purposes of the measurement of potentials, this is equivalent to the requirement that Henry's law, and thus the Nernst equation in concentration form, be obeyed.

Experimentally, in nearly all melts the potential of the Ag(I)/Ag couple varies with the logarithm of Ag(I) concentration at Ag(I) concentrations of at least $10^{-5}$ to $10^{-2}$ mol/dm$^3$. At lower concentrations of Ag(I), the potential deviates from this Nernstian response in a manner which is often nonreproducible and depends upon the melt, its preparation, and its history. At higher concentrations the potential deviates in a reproducible and systematic manner. The deviation at very low Ag(I) concentrations is probably due to the presence of other couples as impurities; their significance increases as the
concentration of Ag(I) decreases because the exchange current, though comparatively high for the Ag(I)/Ag(0) couple, decreases with concentration until it is too low to control the potential. The deviation at high concentration is expected because, as concentration increases, the activity coefficient cannot remain that of the dilute solution which, for a solvent system of fixed nominal composition, is fixed also. Thus the standard state of Ag(I) is a physically unreal state in which the behavior of Ag(I) is that of an ion under conditions of essentially infinite dilution in the solvent system yet at an arbitrarily chosen fixed concentration. This fixed concentration can be selected as unity on the molarity, molality, or mole fraction scale as convenient.

The use of this electrode involves simply the measurement of its potential against any electrode of constant potential over the range of Ag(I) concentrations in which Nernstian behavior is observed. The standard condition is obtained by extrapolation using the Nernst equation to the arbitrarily fixed concentration of unity on the desired concentration scale. The potential of the cell so extrapolated is then assigned to the other electrode of constant potential, since the standard potential of Ag(I)/Ag(0) is defined as zero. It is most convenient to generate a series of increasing concentrations of Ag(I) by anodic coulometry from the Ag metal present using an auxiliary cathode. At low current densities the Faradaic efficiency is 100% within experimental error; the only problem is extensive recrystallization of solid silver metal.

Comparison With Other Reference Electrodes

The reference electrode suggested is already widely used (1). The Ag(I)/Ag couple has the advantages of use of a noble and unreactive metal; a relatively high exchange current; compatibility of Ag(I) with both solvent systems (5) and apparatus materials; low vapor pressure of both components of the couple at high temperatures; operation over a wide temperature range; and definition of the standard state of both components of the couples in a manner which does not vary with melt composition except for solvent systems based on silver salts, which are not a group widely used or studied. Of greater significance is the fact that it can be constructed with a very low junction potential because the solvent system at the reference electrode differs from that elsewhere only in
the presence of a relatively low concentration of Ag(I). A separator required to prevent mixing such as a glass frit, porous ceramic, or glass membrane will therefore develop across itself a junction potential of at most one or two mV, as is observed. Electrodes employing significantly different solvent melt compositions at the reference electrode than at the opposite electrode must necessarily have large, and often ill-defined, junction potentials across their separators.

References

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