Electrode Potentials in Fused Systems X. Measurement of Cation Concentration in Molten Salts Using Glass Membrane Electrodes

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A potentiometric method utilizing glass membrane reference electrodes in a concentration cell for the continuous measurement in situ of molten salt composition is presented. Relevant data for the AgCl-NaCl, AgBr-NaBr, and Ag_2SO_4-Na_2SO_4 systems are given. Using cells of the type

\[ M_1 | M_1A(a_1), M_2A(a_2) | \text{glass} | M_1A(a_1), M_2A(a_2) | M_1 \]

where the \( a \)'s are activities, the unknown mole fraction \( X_2 \) can be calculated from the equation

\[ \log \left( \frac{X_2}{1 - X_2} \right) = \frac{E}{2.303RT/F} - \frac{1}{X_n} \log \left( \frac{1 - X_n}{X_n} \right) \]

where \( t' \) is a concentration-independent constant of the system and \( X_n \) is the concentration of \( M_1A \) in the reference electrode. The method is capable of measuring \( X_2 \) in molten salt with an accuracy of better than 5 percent over a concentration range of \( 10^4 \). Application of the method to cations other than silver is discussed.

Key Words: Analysis, electrodes, glass, membranes, metal ions, molten salts, membrane electrodes.

1. Introduction

Increasing need for reliable reference electrodes in molten salts has led, in recent years, to the development of glass membrane electrodes for use in these media. These electrodes have a number of advantages over electrodes in which a liquid junction is maintained by means of pinholes, asbestos fibers, frits, etc., between the reference and indicator compartments of the cell. They are easily constructed, rugged, and maintain constant potential over relatively long periods of time.

A number of membrane electrode designs, all based on the Ag-Ag^+ equilibrium, have been published [1, 2, 3, 4]. In contrast to aqueous systems in which the glass electrode functions as indicator electrode, primarily for pH measurements, in molten salts it serves as a reference electrode with respect to which potential changes at other electrodes can be observed. For this application the primary requirement is stability and reproducibility, i.e., several electrodes of identical design should vary as little as possible in potential behavior. To be useful in this sense it is not necessary that the potential of such an electrode be known on any thermodynamic scale, e.g., with respect to the \( 1/2 \ Cl_2(g) + e = Cl^- \) equilibrium of the chlorine electrode.

It is by now well known that when a glass electrode is combined with another electrode, either in a concentration or in a chemical cell, the measured emf will differ markedly from the Nernst value except in the special case in which the compositions on both sides of the glass are nearly identical [1]. The reason for this deviation lies in the selectivity of every glass for certain ions in the melt. Thus the ionic transport through the glass is relatively independent of melt composition; this leads to a membrane potential which must be taken into account, in addition to the Nernst value.

We have recently studied the behavior of glass in a variety of molten salt media in order to gain more information on ionic transport in glass [5, 6, 7, 8]. One result of this work is that it is now possible to use glass membrane reference electrodes for the determination of melt composition with respect to certain ions. Using these electrodes the melt composition can be measured continuously without disturbing the system by sampling. The purpose of the present paper is to give a more detailed discussion of those aspects of glass electrodes which pertain to the measurement of melt composition, particularly in the dilute range. We have illustrated this by new measurements of the AgCl-NaCl and AgBr-NaBr systems which were previously measured at higher silver concentrations, and of the Ag_2SO_4-Na_2SO_4 system which has not previously been studied.
We begin by discussing a simple concentration cell

$$M_1 | M_1 A(a_1), M_2 A(a'_1) | \text{glass} | M_1 A(a_2), M_2 A(a'_2) | M_1$$

where the $a$'s represent activities on the mole fraction scale. As shown previously the emf of this cell is

$$E_{\text{cell}} = (RT/F) \ln \frac{a_1}{a_1 - \int_{a_1}^{a_2} \Sigma t_i d \ln a_i}$$

(1)

which is formally also the potential of the cell with liquid junction. The chief difference between membrane and liquid junction potentials is that in the former case (a) only ions transported across the glass are included in the summation, and (b) if the melt contains more than 2 percent sodium, $t_i$ is a constant in any cell and can be taken outside the integral [5]. For systems containing a single anion only cation terms are included in the summation. Since $\Sigma t_i = 1$, eq (1) becomes

$$E_{\text{cell}} = (RT/F)_{M_2} \ln \frac{(a_2/a_1)(a'_2/a'_1)}{(a_2/a'_2)(a'_2/a'_1)}.$$  (2)

Equation (2) is useful for the measurement of an unknown composition only if (a) $t_{M_2}$ is really independent of composition over the entire concentration range, (b) no changes occur in the reference electrode, e.g. composition changes by vaporization, and (c) the thermodynamic behavior of the melt, i.e., the activity coefficients of the components, are known. In a study of several silver halide-alkali halide solutions [5] it was found that (a) is satisfied if the melt contains at least 2 percent sodium, but not if it contains only the larger alkali metal cations. Condition (b) can be satisfied fairly well by using small diameter tubing. For the purpose of measuring melt composition condition (c) imposes a great inconvenience. In that case it is probably preferable to write eq (2) in terms of the mole fractions and to let $t_{M_2}$ absorb the nonideality of the system. Although this treatment can give misleading results if precise information on ion transport in glass is desired [7], it is justified when the purpose of the measurement is the determination of melt composition. In that case it is more convenient to write eq (2) in terms of the mole fraction, viz

$$E_{\text{cell}} = (RT/F)_{t'} \ln \frac{(X_2/X_1)(X'_2/X'_1)}{(X_2/X'_1)(X'_2/X'_1)}.$$  (3)

where

$$t' = t_{M_2} \left\{ \frac{\ln \left( \frac{X_2}{X_1} \frac{X'_1}{X'_2} \right)}{\ln \left( \frac{X_1}{X'_1} \frac{X'_2}{X'_2} \right)} + 1 \right\}$$  (4)

and the $Y$'s are the Raoult's law activity coefficients of the components. Making use of $X_1 + X'_1 = X_2$

$$+ X'_2 = 1$$

$$E_{\text{cell}} = (RT/F)_{t'} \ln \frac{(X_2/X_1)(1 - X_1)/(1 - X_2)}{(1 - X_2)/(1 - X_1)}.$$  (5)

t' can then be regarded as the empirical slope obtained in a calibration run when $E_{\text{cell}}$ is plotted against $(RT/F) \ln [(X_2/X_1)(1 - X_1)/(1 - X_2)]$. In practice, it is most convenient to keep one side fixed as a reference and to vary the composition of the other side. Once $t'$ has been determined for a particular melt and glass it can then be used in eq (5) to determine unknown concentrations in this system. For example if $X_1 = X_R$, the reference composition, eq (5) can be written

$$\log \left( \frac{X_2}{1 - X_2} \right) = - \frac{E}{2.303(RT/F)t'} - \log \left( \frac{1 - X_R}{X_R} \right).$$  (6)

For dilute melts $1 - X_2 = 1$.

2. Experimental Part

The general procedure has been outlined previously [4]. Some changes and refinements are discussed below. All experiments were carried out in alumina crucibles open to the atmosphere to duplicate more probable conditions of use.

2.1. Reference Electrodes

Preparation and pretreatment of the glass tubes and silver wire have been described [4]. The reference melt was prepared by melting appropriate quantities of the silver and sodium salts to give ~10 mole percent silver. This concentration appears to be suitable for both higher and lower unknown concentrations and minimizes the corrosion of the silver wire [8]. It proved most useful to make up 50 to 100 g of this composition at one time and then use 2 to 3 g of it in each electrode. Since microcrystalline segregation occurs in these melts on cooling (see below) the quenched melt was ground to a fine powder before use. Several representative portions were analyzed by electrodeposition. The precision of the analytical method was better than 1 percent.

2.2. General Procedure

Two identically prepared reference electrodes were placed in an alumina crucible containing ~120 g of the sodium salt and heated to the desired temperature. Weighed amounts of the corresponding silver salt were added. Emf's were measured between a 30 mil bare silver wire in the melt and each of the reference electrodes, as well as between the two reference electrodes, using a Leeds and Northrup K-3 potentiometer and electronic galvanometer. The melt, open to the atmosphere, was continually stirred with a stream of dried helium passing through a 4-hole ceramic tube.

In unstirred or insufficiently stirred melts the emf
was always lower, indicating that a layer of higher silver ion concentration surrounds the indicator electrode. The effect is most pronounced in dilute solution and decreases with rising concentration. With increasing stirring rate the emf increases to a limiting value. We assume that this emf then corresponds to that for the bulk melt.

In our initial experiments samples of the melts were taken by dipping a cold ceramic rod and quickly withdrawing it. Analyses of the samples frozen on the rod gave increasingly lower concentrations of silver than the values calculated with a constant transport number as the total silver concentration increased. In other words, if the analytical values are used to calculate transport numbers, these latter decrease markedly as the silver content of the melt rises. These observations are explicable in terms of the phase diagrams of various silver-alkali salts published by Zemczuzy [9]. He showed that in these systems the solid phase is always poorer in silver than the liquid in equilibrium with it. The difference increases with rising silver concentration. Apparently then, the liquid composition cannot be frozen into the solid even by rapid quenching. Consequently, samples for analysis were obtained by dipping a 2 ml platinum bucket attached to a long heavy platinum wire into the melt, equilibrating its temperature with the melt, withdrawing samples and pouring these as rapidly as possible onto a heavy metal tray. This procedure was repeated as many times as necessary to obtain a sufficient sample for analysis. Alternatively, samples were piped into a 9 mm wide fused silica tube equilibrated with the melt and poured into the tray. Samples were taken after the emf had been steady for at least 15 to 20 min. The temperature was measured with a chromel-alumel thermocouple which was placed into a glass tube immersed directly in the melt. Temperatures are estimated to be accurate to within ±1°C.

2.3. Sources of Error

a. Stability and Reproducibility of Reference Electrodes

No extensive stability tests were carried out. However, we found that some electrodes kept in the melts in the 800 to 900 °C range for more than 8 to 10 hr began to deviate increasingly from newly immersed electrodes. This effect appears to be greater in the halides than in the sulfate. Since these electrodes are so easily and cheaply constructed we regard them as the “throw-away” type and suggest replacing them every 8 to 10 hr. The potential between identically prepared reference electrodes immersed in the same melt varies randomly, but never exceeds 2 mV, this larger difference occurring in the sulfate system. In the halides the difference was usually a few tenths mV. For the determination of actual concentrations the limit of useful measurement is ~1 mV; for relative measurements of concentration ratios or rates of change, e.g., in kinetic studies [8], measurements are significant to ~0.1 mV.

b. Indicator Electrode Errors

The lower limit of measurable silver ion concentration is imposed by the nearly instantaneous corrosion of the indicator electrode in alkali metal salts. Thus, if an emf is measured between the reference and a bare silver wire in a pure alkali metal salt the calculated silver ion concentration is never lower than 10⁻⁵ [8]. This is presumably the concentration near the metal surface and not bulk melt composition.

Concentration gradients which build up near the electrode in dilute solution in unstirred melts require good stirring if the bulk composition is to be measured, the difference in emf of stirred and unstirred melts, can easily amount to 20 mV.

As the melt composition approaches that of the reference the emf decreases to zero. It is clear from eq (6) that the accuracy of the measurement must also decrease due to loss of significant figures from E since the uncertainty of the measurement remains fairly constant. It is thus advisable to use a reference composition which differs sufficiently from the melt to be measured to give an emf of ~0.1 V.

We illustrate the effect of several errors by calculating the consequence of these on the measured concentration. Since these errors differ somewhat for high and low concentrations, one example of each is given.

Nominal values: \( X_R = 0.100, \ t' = 0.95 \)
\( T = 1123 \) K
Case I: \( E_{cell} = 0.300 \) V \( X_2 = 0.7437 \)
Case II: \( E_{cell} = -0.400 \) V \( X_2 = 1.435 \times 10^{-3} \)

<table>
<thead>
<tr>
<th>Error</th>
<th>( X(I) )</th>
<th>( \Delta X(I) )</th>
<th>( X(II) \times 10^3 )</th>
<th>( \Delta X(II) \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta t' = 0.01 )</td>
<td>0.7398</td>
<td>0.0041</td>
<td>1.473</td>
<td>0.053</td>
</tr>
<tr>
<td>( \Delta X_R )</td>
<td>.0001</td>
<td>.7429</td>
<td>.0020</td>
<td>1.450</td>
</tr>
<tr>
<td>( \Delta E = .001 )</td>
<td>.7437</td>
<td>.0020</td>
<td>1.429</td>
<td>.010</td>
</tr>
<tr>
<td>( \Delta T = 2^\circ )</td>
<td>.7427</td>
<td>.0019</td>
<td>1.449</td>
<td>.008</td>
</tr>
</tbody>
</table>

On the basis of the above calculation the accuracy of the method is estimated to be approximately 1 percent for fairly concentrated solutions, and 5 percent for dilute \( (10^{-4} < X_2 < 10^{-3}) \) ones. Since the major source of error results from uncertainties in \( t' \) it is important that the calibration run be carried out carefully. In particular, the melt compositions in the calibration must be accurately known. The required accuracy can be obtained by careful weighing of the components for silver-rich melts; for melts dilute in silver it is important that a representative sample of the liquid composition is obtained for analysis (see above).
3. Results

Plots of eq (5) for the three systems of this study are shown in figure 1. The origin of course represents $X_1 = X_2 = 0.1$. (Slightly different reference compositions were used in the three systems.) The fact that all three plots pass through the origin shows that asymmetry potentials are absent. The range of concentration represented by the plots is $10^{-4} < X_2 < 10^{-1}$. For each of the three systems the plot is linear, i.e., $t'$ is constant over this range. The small differences in the slopes probably arise from differences in the activity coefficient terms. Combined with the data of previous studies [4, 5], these results show that the method presented in this paper is capable of measuring the silver ion concentration in $\text{Ag}^+ - \text{Na}^+$ melts over a range of $10^4$. The values of $t'$ and its standard deviation for the systems studied are

<table>
<thead>
<tr>
<th>System</th>
<th>$t'$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AgCl} - \text{NaCl}$</td>
<td>1.148</td>
<td>0.0034</td>
</tr>
<tr>
<td>$\text{AgBr} - \text{NaBr}$</td>
<td>1.009</td>
<td>0.008</td>
</tr>
<tr>
<td>$\text{Ag}_{2}\text{SO}_4 - \text{Na}_2\text{SO}_4$</td>
<td>0.965</td>
<td>0.011</td>
</tr>
</tbody>
</table>

$t'$ is independent of temperature between 800 and 900 °C [4]. A previous comparison between Vycor and Supremax [2, 4], two glasses of quite different composition, indicates that $t'$ is nearly independent of the particular glass used.

4. Conclusions

A potentiometric method has been presented which utilizes glass membrane reference electrodes in a concentration cell arrangement for the continuous measurement of molten salt composition in situ with respect to certain ions.

The method was illustrated by measurements of three melts containing silver and sodium ions. However, the principles which are involved are applicable to other ions as well. For example, data on the CuCl-NaCl system have already been obtained [7]. Thus it should be possible to measure the concentration of any metal ion for which a reversible electrode can be constructed. At present the method appears to be limited to melts containing at least 2 mole percent sodium ion. Another limitation of the method is that the formation of insoluble oxides on and any appreciable corrosion of the metal wires used in the reference and indicator electrodes must be avoided. In some cases this may require an inert atmosphere over the measurement part of the system. In studying any particular system the applicability of the method must be tested and a calibration curve of the type shown in figure 1 constructed.

5. References


(Paper 69A6-379)
Selected Abstracts


The calorimetric method for determining the chemical formula and the instability constant of a complex ion involves the determination of the partial molal heat effects resulting from the separate addition of increments of each of the constituents of the complex to a complete range of mixtures of the constituents. The general mathematical derivations necessary for the utilization of the method have been developed, and the complex copper cyanides have been used as an example. The instability constants for the Cu(CN)\(_2\)\(^-\) and the Cu(CN)\(_3\)\(^{3-}\) ions were found to be 1.0 \(\times\) 10\(^{-3}\) and 2.3 \(\times\) 10\(^{-3}\) respectively.


The mass spectrum of vapor in equilibrium with anhydrous yttrium chloride was examined by a Knudsen effusion technique between 800\(^\circ\) and 1000 \(\circ\). Ions due to monomeric and dimeric vapor molecules were identified. Heats of evaporation and sublimation for the two species are: dimer H\(_2\) \(\times\) 86 kcal/mol, H \(\times\) 74 kcal/mol; monomer H\(_2\) \(\times\) 57 kcal/mol, H \(\times\) 47 kcal/mol.


A new method for the adjustment of vibrational force constants is presented. It avoids some of the divergence difficulties which may be encountered in perturbation and least-squares procedures. The new method employs an efficient computer program to adjust an initial set of force constants in accordance with the requirement that each successive adjustment leads to a smaller sum of squared deviations between calculated and observed eigenvalues. Several variants of the procedure are given, and their application to a number of actual cases is discussed in detail.


An asphalt flux of southeastern United States origin was treated with various oxides of nitrogen as the oxidizing gases. Changes in physical and chemical properties were measured by infrared spectroscopy, softening points, and microviscometry. Reaction temperatures did not exceed 166\(^\circ\)C. and gas flow rates were well below those used in the commercial air-blowing of asphalts. Nitrous oxide and nitric oxide, alone, gave very little reaction. Nitrogen dioxide, photosensitized nitrogen dioxide, and a nitric oxide-oxygen mixture reacted with the asphalt flux to produce coating-grade asphalts. The reaction time needed to produce a given asphalt softening point with photosensitized nitrogen dioxide, for example, was 1/20 that needed for air alone. Coating-grade asphalts made with oxides of nitrogen were more stable to photooxidation, and to film rupture at any given rate of shear, than was the commercial asphalt from the same flux. A correlation was observed between the extent of photooxidation of exposed asphalts and the changes in viscoelastic properties.


The photolysis of C\(_2\)H\(_6\) in liquid nitrogen was studied at 1470 \(\AA\). It was found that the excited ethylene so produced, whose alternative paths are collisional deactivation and decomposition to acetylene plus hydrogen, was entirely deactivated by nitrogen with the acetylene quantum yield falling to zero at very low conversion.

\[ C_2H_6 \rightarrow C_2H_4 + H_2 \]

\[ C_2H_4 + M \rightarrow C_2H_4 + M \]

The excited ethane formed in the primary process is not deactivated by \(10^5\) collisions per second with nitrogen. Excited ethylene formed by photolysis of ethylene at 1470 \(\AA\) is not quenched by the nitrogen but is partially quenched by .001 mole % NO. Thus, electronically excited ethylene is partially deactivated by collisions at a rate of \(10^5\) sec\(^{-1}\). No positive evidence for reaction of CH\(_2\)CH with N\(_2\) was obtained.


Selected P-p-T data for liquid and gaseous neon have been fitted with a function. The selected data are the available experimental data, supplemented in regions of pressure and temperature where experimental data are not available by values calculated from the theory of corresponding states and a generalized equation of state. Deviation plots are given which indicate the accuracy with which the analytical function represents the experimental data. The equation of state and the zero pressure specific heat were used to calculate tables of density, entropy, and enthalpy for selected temperatures and pressures. These properties are also illustrated in temperature-entropy diagrams.


Field emitters oriented with a prescribed plane perpendicular to the emitter axis can be prepared simply and economically. This involves the use of the spark erosion technique to machine the emitter blanks from a single crystal rod that may be as small as 1/8\(^\prime\) diameter. The method is described in detail, and examples of 100 and 111 oriented tungsten emitters are shown.


A statistical-mechanical treatment of a polymer molecule adsorbed on a solid surface is given. The surface coverage of adsorbed molecules is assumed to be sufficiently low that the interactions of the adsorbed polymer molecules with each other may be neglected. The partition function is derived for a polymer molecule with sequences of repeating units adsorbed at an interface and with other sequences (loops) held at the surface only at their ends. The assumption of Gaussian statistics for the loops leads to a formulation equivalent to that used for the helix-coil region in DNA molecules. A broad distribution of loop sizes is found, in contrast to Silberberg's theory in which a sharply peaked distribution is assumed. The latter theory predicts also small loops for all values of the adsorption free energy. In contrast, our theory predicts large loops and few units adsorbed for small adsorption free energies and small loops and more units adsorbed for larger adsorption free energies when the chains are sufficiently flexible. This result is also in partial agreement with earlier theories that predict large loops, even for relatively large adsorption free energies. On the other hand, our theory predicts only a small number of loops and most units at the surface for stiff chains. A relationship between the initial slope of an adsorption isotherm and the molecular weight of the polymer is presented.

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The spin-lattice approach to equilibrium is studied for situations in which the “lattice” heat capacity, is not infinite. It is assumed that the spins and the “lattice” each have a well-defined temperature and that the bath either has been removed or is only very weakly coupled to the lattice. It is shown that asymptotically the magnetization relaxes exponentially with a relaxation time which can be very much different from T1 (the spin-lattice relaxation time for an infinite lattice heat capacity), not only in numerical value but in its functional dependence upon temperature, magnetic field, and spin concentration. Some examples are presented in which the effect of the finite lattice is to “lock” the magnetization in at its initial value for times one to two orders of magnitude longer than the ultimate relaxation time.


The transmission of electrons through the rare gases and mercury vapor has been examined as a function of electron energy, with energy resolution of about 0.04 eV. Many anomalies (resonances) localized in energy have been observed, totaling eleven in helium, six in neon, two each in argon, krypton, and xenon, and five in xenon and thirteen in mercury. The interpretation of these resonances in terms of compound negative ion formation is discussed, and in several cases electron configurations are assigned to the negative ions. In helium, neon, xenon, and mercury, sharp decreases in transmission are observed which are attributed to the onset of inelastic processes. Definite identification of the inelastic processes in the case of helium enables calibration of the absolute electron energy scale to within ±0.03 eV.


A theoretical examination of the electronic energy bands of cubic strontium titanate has been performed by application of the LCAO (linear combination of atomic orbitals) method. Diagonal energies were determined from ionization potentials and crystalline fields based on a point charge model for the ions. The ionic charges were adjusted to give agreement with the observed energy gap. Overlap integrals were estimated from free ion wave functions. For the crystals studied, the calculations led to filled valence bands derived primarily from oxygen 2p orbitals and empty conduction bands derived predominantly from titanium 3d orbitals. In cubic strontium and barium titanates, there are six lowest conduction band ellipsoids lying along <100> directions of k-space with minima probably at the edges of the Brillouin zone. The longitudinal mass is about 20-50 m0 and the transverse mass about 1 m0. Spin-orbit splitting removes degeneracy at k=0 and leads to additional conduction bands several hundreds of an electron volt above the lowest conduction band. Comparison is made with experimental data on conductivity, Hall effect, thermoelectric power, reflectivity, and soft x-ray emission. Results are in substantial agreement with experiment.


Levels of He, at 57.1 and 58.2 and of Hg, at 4.0, 4.2, and 4.8 eV, whose observation is described in an accompanying paper, are identified spectroscopically as 2S2p 3P, 2S2p 3P, 6S6p 3P, and 232P3D, respectively. The identification procedure, which combines elements of spectroscopy and collision theory is described.


The Ginsburg-Landau equations are modified to include a magnetic permeability which varies with the order parameter χ according to the relation: μ = μ0 + μ1(1 - χ). The influence of this on the predicted behavior of a superconducting film in a tangential magnetic field is investigated theoretically. A new value is derived for the upper limit of the critical field for a bulky superconductor and a thin film.


An interpretation of the mechanism of ion-atom collisions is presented and discussed.


Mass spectrometric techniques have been used to obtain the photoionization efficiency curves for H2, HD, and D2 in the energy range 815 to 700 A (15.2 to 17.7 eV). A qualitative description of the observed autoionization process, based on a theory proposed by Fano, is applied to an analysis of the results.


The existence of multiple band conduction in n-type rutile for temperatures above ~40 K is deduced from studies of the Hall coefficients and electrical conductivities from ~2 to 600 K. This investigation emphasizes the anisotropy of the Hall coefficients, i.e., the Hall effect measured with magnetic fields along the a- and the c-axis, respectively (R<sub>a</sub> and R<sub>c</sub>). The pronounced temperature dependence of the ratio of these two coefficients can most easily be interpreted on the basis of two competing conduction processes. Measurements on samples with widely differing charge carrier concentrations prove that the conduction processes involved are due to intrinsic energy states of the crystal. The energy separation between the lowest conduction band and the bottom of the next higher one is calculated to be 0.05±0.01 eV, where the indicated uncertainty denotes estimated limits of error. These concepts are consistent with recent band structure calculations. Impurity and surface conduction are shown to be negligible.


In this note we comment on the use of analytical functions to describe the behavior of a system in the critical region, as proposed by Ulybin and Malyshenko, among others. We also investigate an apparent sharp disagreement noted by these authors between density gradients obtained optically and those derived from P-V-T data, in the critical region. We think that much of the disagreement arises from the way the P-V-T data were analyzed. We conclude that in the critical region the pressure versus density isothersms are much flatter than has been inferred from P-V-T work. The consequent large gravitational effect together with the difficulty of determining the slope of the isotherm severely limit the use of P-V-T measurement for the investigation of detailed behavior of thermodynamic quantities in the vicinity of the critical point.


Corrections to the Lorentz-Lorenz equation for the refractive index of a fluid have been evaluated, near the critical point using Yvon’s statistical mechanical theory of the refractive index, together with the Ornstein-Zemike asymptotic form of the two-particle correlation function. For argon, with reasonable values for the numerical parameters, the correction is smaller than one part in 10<sup>6</sup>.


Published experimental infrared reflection data are analyzed to obtain information about the long wavelength polar modes of lattice vibration in rutile (TiO<sub>2</sub>). Weighted sums of squares of effective charges are found, and are compared with the same quantities calculated on a simple ionic model. The continuum polarization model of electron-phonon interactions is extended to apply to crystals with several types of longitudinal polar phonons, and the results are used to discuss polaron theory in rutile.

Using the method described in an article on rutile (D. M. Eagles, to appear), the author has calculated the long wavelength longitudinal polar mode frequencies and coupling constants in SrTiO₃.

Pressure dependence of the internal field at the Co⁶ nucleus in a 99.5% Ni-0.5% Co alloy, L. H. Bennett, J. Appl. Phys. 36, No. 3, Pt. 2, 942–943 (Mar. 1965).

The room temperature nuclear magnetic resonance absorption of Co⁶ in an alloy of 0.5 percent Co in Ni has been measured under hydrostatic pressures of up to 7 kbars. This is in the same direction (increasing frequency for increasing pressure), as for Ni⁶ in Ni. The ratio of the resonance frequency to the change in frequency with pressure \( \rho/p = 159.5 \text{ Hz/bar} \). Values in this is in the same direction (increasing frequency for increasing pressure) as for Ni⁶ in Ni. The internal field at the Co⁶ nucleus decreases with increasing temperature more slowly than that at the Ni⁶ nucleus in Ni-rich Ni-Co alloys. This discrepancy in the temperature dependences remains as large, when plotted at constant volume, as it was at constant pressure.


Electrodeposited lead dendrites were grown and examined by x-ray diffraction and metallographically. Their structure was essentially that of two crystals having a twist relation about a common [111] pole which was normal to the flat surface of the two dimensional dendrites. Each dendrite contained many small voids or channels. The direction of growth was either about halfway between a <211> direction of one crystal and a neighboring <211> direction of the second crystal or halfway between <110> direction.


SU(6) Clebsch-Gordan coefficients for the product 35 × 56 have been calculated. They have been used to predict a new set of scattering amplitudes which relate widely different final states for reactions in which mesons are incident on proton targets.


The use of hydrogen in space vehicles and in nuclear devices demands the accurate knowledge of its mechanical and thermal properties. As mechanical properties of parahydrogen nearly 1200 closely spaced P-T points have been measured between 14 and 100 \(^{\circ}\)K and between 2 and 350 atm. The P-T surface was approximated by a large number of polynomials coupled with appropriate interpolation schemes. Use of the virial expansion allows extrapolation to pressures below 2 atm.

Thermal properties may be obtained after relating the experiment above to a second one in which the heat capacity at constant volume was determined for a variety of experimental conditions. At temperatures below critical these heat capacities are used as primary data, while at temperatures above critical they serve as check on the correlation between the statistically calculated specific heats and the P-T data. Further tests of the correlation arise when calculating thermodynamic functions. From this correlation it is now possible to compute as function of pressure and temperature such quantities as specific volume, enthalpy, entropy, specific heat at constant volume, specific heat at constant pressure, sonic velocity, the Joule-Thomson coefficient and the heats of vaporization.


A new expression is suggested to account for the variation with pressure of the spectral intensity distribution in microwave absorp-

tion lines of gases, with specific application to the ammonia inversion spectrum. This expression departs from the conventional Van Vleck Weisskopf expression by adding a new coupling parameter which is proportional to the gas density. The theory is tested by applying it to the oblique Brewster and of Birnbaum and Maryott on ammonia.


The infrared emission spectra of HBr²⁹ and HBr⁸¹ have been observed by exciting HBr in an electric discharge. Lines in the 1–0, 2–1, and 3–2 bands have been measured to an accuracy of the order of 0.01 cm⁻¹. Pure rotational transitions of HBr²⁹ and HBr⁸¹ which were not resolved have also been observed and measured with an accuracy of the order of 0.2 cm⁻¹. Values are reported for \( \omega_e, \omega_q, \omega_{e'q}, \) (only limits for this constant), B_e, D_e, a_e, b_e, c_e, and \( \delta_e \) and approximate values of \( \tilde{H}_0 \) and \( \tilde{H}_1 \) are also obtained. The results are found to be in agreement with Dunham’s theory. Values of the potential constants \( a_1, a_2, a_3 \) are calculated. The B-values for HBr²⁹ and HBr⁸¹ agree with calculations based on micro-wave measurements of DBr²⁹ and DBr⁸¹.


Photoionization efficiency curves for the molecule and fragment ions of CH₄ and CD₄ are obtained in the wavelength region 1000 to 600 Å. The electronic structure of the molecule ion is related qualitatively to the shape of the parent ionization efficiency curve and the implications of the complicated vibronic behavior of the CH₄ ion are discussed. A qualitative explanation is given for the observed isotope effect on the parent ionization efficiency curve and on the fragment ion threshold energies. More nearly correct values of \( I(CH_4) = 12.71 \text{ eV} \) and \( I(CH_4) = 12.87 \text{ eV} \) are obtained. Other thermochemical values deduced from the study are: \( D(CH_4 - H) = 4.41 \text{ eV}, D(CH_4 - D) = 4.55 \text{ eV} \), \( D(CH_3 - H) = 4.87 \text{ eV} \), and \( H(CH_4) = 4.87 \text{ eV} \). Zero-point energy differences for methyl and methylene ions and neutrals are also estimated.


This paper is a review of the phase equilibria data available on binary systems containing a rare earth oxide, Y₂O₃ or Sc₂O₃, as one component. The review is limited to the oxides of the trivalent rare earth ions only. The phase diagrams are shown when previously published and unit cell dimensions of all compounds are also given where known. From a discussion of the problems involved in the accurate measurement of high temperatures it is concluded that accurate melting point standards are needed for the temperature range 2000–2400 °C in air.


This is a brief communication addressed to the Editor of the Journal of the Electrochemical Society briefly discussing the value of the Faraday.

Other NBS Publications

J. Res. NBS 69B (Math. and Math. Phys.), No. 3 (July-Sept. 1965), 75 cents.


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Some \( L_2 \) Markoff inequalities. L. F. Shampine.

Some theorems on the permanent. R. A. Brualdi and M. Newman.

On Kirchhoff’s law and its generalized application to absorption and emission by cavities. F. J. Kelly.

On a relation between two-dimensional Fourier integrals and series of Hankel transforms. J. V. Cornecho and R. P. Soni.

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On convex metrics. C. Witzgall.

Some extensions of Banach’s contraction theorem. P. R. Meyers.

A variant of the two-dimensional Riemann integral. A. J. Goldman.


A primal (all-integer) integer programming algorithm. R. D. Young.


Some applications of the wave front shearing interferometer. J. B. Saunders.

Precision method for evaluating primary aberrations of lenses with a Twyman interferometer. J. B. Saunders.

Comparators for voltage transformer calibrations at NBS. W. C. Sze.

Voltage dependence of precision air capacitors. J. Q. Shields.

Single crystal x-ray diffraction at high pressures. C. Weir, S. Block, and G. Piermarini.


Stress analysis of tape-wound magnet coils. J. Hord.

Centerline correction for precision roughness specimens. J. L. Chamberlin.


“Ultra Low Frequency Electromagnetic Fields” Papers


Solar wind and its interaction with the magnetosphere. C. P. Sonnett.

Schumann resonances. J. Galejs.

Earth-ionosphere cavity resonances and the propagation of ELF radio waves. J. R. Wait.


Experimental results on the dynamics of the F region. W. Becker, R. Rüster, and J. Klostermeyer.

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Preliminary results of a micropulsation experiment at a conjugate points. R. E. Gendrin and V. A. Troitskaya.

Some characteristics of geomagnetic pulsations at frequencies near 1 c/s. W. H. Campbell and E. C. Stiltener.

Propagation of hydromagnetic waves in the magnetosphere. M. Sugiiura.

Ionospheric perturbation (the roles played by the ionosphere in geomagnetic pulsations). S. Matsushita.


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Ground-based passive probing using microwave spectrum of oxygen. E. R. Westwater.


Effects of rocket outgassing on rf experiments. W. Pfister and J. C. Ulwick.


Measurement of group velocity of 17.8-kHz VLF radio waves. W. D. Westfall.

On the radio noise level at low and very low frequencies in polar regions. T. Stocklet Jørgensen.

Experimental study on the circular loop antenna immersed shallowly in a conducting medium. Keigo Lizuka.

Directivity of uniformly spaced optimum endfire arrays with equal sidelobes. M. T. Ma.

Extension of Fock theory for currents in the penumbra region. V. H. Weston.


Scattering resonances of a cylindrical plasma. W. M. Leavens.


Atmospheric radio noise bursts in the LF band at Bangalore. S. V. C. Aiya and K. N. Lakshminarayan.


Model experiments on propagation of groundwaves across an abrupt boundary at perpendicular incidence. R. J. King and S. W. Maley.


An anisotropic electron velocity distribution for the cyclotron absorption of whistlers and VLF emissions. H. Guthart.

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Interference rejection capability of a switched radiometer. R. E. Clapp.

Atmospheric breakdown limitations to optical maser propagation. R. G. Tomlinson.

Phase steps and amplitude fading of VLF signals at dawn and dusk. D. Walker.


Comments on H. Volland’s “Remarks on Austin’s Formula.” J. R. Wait.

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I Session: Jupiter, as observed at long radio waves.

II Session: Jupiter, as observed at short radio waves.

III Session: Passive radio observations of Venus, Saturn, Mercury, Mars, and Uranus.

IV Session: Passive radio observations of the Moon.

V Session: Radar observations of the planets.

VI Session: Radar observations of the Moon.


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