

Table III: Summary of Specific Conductance and Equivalent Conductance of NaNO_3 at 369° under He Pressure

Saturating pressure, P_{He} , atm.	Specific conductance, κ_{He} , $\text{ohm}^{-1} \text{cm}^{-1}$	Density, ^a d_{NaNO_3} , g. cm.^{-3}	Equiv. conductance, Λ_{He} , $\text{cm}^2 \text{ohm}^{-1} \text{equiv.}^{-1}$
419	1.191	1.891	53.52
334	1.201	1.888	54.07
162	1.215	1.881	54.89
97	1.222	1.879	55.28
0	1.230 ^b	1.875	55.75
232	1.208	1.884	54.50
55	1.225	1.877	55.47

^a Density values are for the pure liquid salt under piston pressure only. ^b This value, interpolated for 369° from published data (see footnote b in Table II) gave the cell constant 343.7 cm.^{-1} .

For He

$$\kappa_{\text{He}} = (1.230 \pm 0.001) - (9.19 \pm 0.25) \times 10^{-5} P_{\text{He}} \text{ ohm}^{-1} \text{cm.}^{-1} \quad (5a)$$

$$\Lambda_{\text{He}} = 55.76 - 5.26 \times 10^{-3} P_{\text{He}} \text{ cm}^2 \text{ohm}^{-1} \text{equiv.}^{-1} \quad (5b)$$

The errors in eq. 4a and 5a are the least-squares standard deviations. No errors are given for eq. 4b and 5b since, as stated, the errors in Λ are probably several per cent at the higher pressures, and furthermore are not able to be obtained accurately from this work. These equations for Λ are included only to indicate the approximate values taken by this quantity.

Discussion

Two causes apparently bring about the observed diminutions of specific conductance, namely that of pressure alone and that of gas solubility in the melt. The large difference between the slopes of the Ar and He isotherms in Figure 3 leaves no doubt that there is a solubility effect under the conditions of this experiment. If pressure is assumed to act linearly on conductance (speaking empirically), then we can conclude that the solubility of Ar or He linearly affects specific conductance as well, at least over the range studied. Since the effect of pressure alone should be the same regardless of the gas employed, the difference between the slopes in Figure 3 will reflect the relative effects of the solubility of Ar and He on conductivity. Evaluation of the absolute effects of solubility will have to await results of ordinary piston pressure studies.^{22,23}

The striking feature brought out by this work is that while He is slightly more soluble than Ar in NaNO_3 ,

the effect of Ar solubility on specific conductance is noticeably greater than that of He. We believe that an explanation of these results may be based on dilution effects by the dissolved gas, and on the different degrees by which some Ar or He atoms may block ionic migration by virtue of their atomic sizes.

According to the hole theory, the distribution function for hole radii, $F_h(r)$, is given as²⁴

$$F_h(r) = Br^6 \exp(-4\pi r^2 \gamma / kT) \quad (6)$$

where B is a constant characteristic of the temperature and surface tension, γ , and r is the radius of a hole. If the radius of a He atom is taken as 1.22 \AA , and that of Ar is 1.92 \AA ,²⁵ then appropriate integrations of eq. 6 reveal that the fraction of holes larger than a He atom is about four times greater than the corresponding fraction referred to an Ar atom. Thus, if the noble gas atoms dissolve by predominantly occupying *existing* liquid free volume as holes, then the solubility of He should be nearly four times greater than that of Ar. If the He atom is even smaller this ratio becomes still larger. Such is not the case observed here, the Henry's law constant for He being only about 25% greater than that of Ar. We tentatively conclude, therefore, that at least a sizable fraction of the gas atoms dissolve by creating their own holes, while the rest may still occupy some existing liquid free volume. In addition, an ion-induced dipole interaction of the polarizable Ar with the ions may serve to enhance the solubility of this gas somewhat.

Since portions of the dissolved inert gas atoms apparently occupy holes of their own creation, part of the specific conductivity changes may be due to a difference between the extents of dilution of the salt by Ar and He. Part of this dilution effect with Ar might well be the result of displacement of NO_3^- ions by the Ar atoms in view of their similar sizes (radius of Ar is 1.92 \AA , that of NO_3^- is 2.3 \AA .²⁶) and the fact that the transport number of NO_3^- has been reported (controversially) as 0.3 in this melt.²⁶ This could help to account for the greater effect of Ar solubility on κ . Also, some of the solute gas molecules may still occupy existing free volume as holes in the melt. In this case a large Ar atom in such a hole could be more effective in "blocking" the jump of a small Na^+ ion (radius of

(23) C. A. Angell, private communications to J. L. C., 1965.

(24) F. H. Stillinger in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, New York, N. Y., 1964, Chapter on "Equilibrium Theory of Pure Fused Salts."

(25) M. Blander, W. R. Grimes, N. V. Smith, and G. M. Watson, *J. Phys. Chem.*, **63**, 1164 (1959).

(26) B. R. Sundheim in "Fused Salts," B. R. Sundheim, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964, Chapter 3.

0.95 Å.²⁶) than could a much smaller He atom in a hole of similar size.

Summary

The lack of a great solubility difference between Ar and He in molten NaNO_3 leads to the conclusion that many of the dissolved gas atoms occupy holes of their own creation in the liquid, while other atoms may still occupy existing free volume. The difference in the solubility effects on specific conductance may be interpreted in terms of (1) a greater dilution effect by Ar than by He, and (2) more effective blocking of ionic jumps by large Ar atoms than by smaller He atoms. As accurate density data for the gas saturated melt at various pressures become available, it conceivably

may be found that the *equivalent* conductance isotherms corresponding to Figure 3 have more nearly the same slope. This, of course, would support the dilution mechanism as being the dominant effect.

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