

Effect of Inert Gas Pressure and Solubility on Fused Salt Conductance. I.

Argon and Helium with Sodium Nitrate¹

by James L. Copeland and Walter C. Zybko

Department of Chemistry, Kansas State University, Manhattan, Kansas 66504 (Received July 20, 1965)

The solubilities of Ar and He in fused NaNO_3 at 369° have been determined to pressures of 451 atm. for Ar and 321 atm. for He. Henry's law constants are $K_{\text{Ar}} = (17.2 \pm 1.7) \times 10^{-7}$ mole of Ar (cm^3 of melt) $^{-1}$ atm. $^{-1}$ and $K_{\text{He}} = (22.7 \pm 0.7) \times 10^{-7}$ mole of He (cm^3 of melt) $^{-1}$ atm. $^{-1}$. Specific conductance, κ , of the melt at the same temperature has been determined under pressures of Ar, P_{Ar} , to 443 atm. and of He, P_{He} , to 419 atm. This conductance decreases linearly with increasing pressure of either gas. Least-squares relationships are, for Ar: $\kappa_{\text{Ar}} = (1.228 \pm 0.002) - (1.94 \pm 0.06) \times 10^{-4} P_{\text{Ar}}$ ohm $^{-1}$ cm. $^{-1}$; and, for He: $\kappa_{\text{He}} = (1.230 \pm 0.001) - (9.19 \pm 0.25) \times 10^{-5} P_{\text{He}}$ ohm $^{-1}$ cm. $^{-1}$, where pressures are in atmospheres. The slightly greater solubility of He and the noticeably larger effect of Ar solubility on conductance are interpreted in terms of the greater part of solute gas molecules creating their own holes in the melt and thereby diluting the salt to different extents. A smaller contribution to the difference in solubility effect may be due to some solute particles still occupying existing free volume in the liquid, the larger Ar atom then causing a more effective blocking of ionic jumps than does the small He atom.

Introduction

Of the several liquid structure theories currently applied to molten electrolytes, the liquid free volume model, as developed by Cohen and Turnbull,² and the hole model, originated by Altar³ and developed by Fürth,⁴ appear to have met with greater success in the explanation and prediction of transport phenomena in simple fused salts. Bockris and Richards were the first to apply the hole model specifically to molten salts.⁵ The subsequent work of Bockris and co-workers, especially in explaining diffusion phenomena in terms of the hole model, has tended to cast favorable light on this theory.⁶⁻¹¹ Similarly, for example, the work of

Angell on conductance-diffusion phenomena in glass-forming melts has served to place the liquid free volume model in good stead.¹²⁻¹⁴ However, there are similari-

(1) This paper was presented in part at the first Midwest Regional Meeting of the American Chemical Society in Kansas City, Mo., Nov. 1965.

(2) M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **29**, 1049 (1958); **31**, 1164 (1959).

(3) W. Altar, *ibid.*, **5**, 577 (1937).

(4) R. Fürth, *Proc. Cambridge Phil. Soc.*, **37**, 252, 276, 281 (1941).

(5) J. O'M. Bockris and N. E. Richards, *Proc. Roy. Soc. (London)*, **A241**, 44 (1957).

(6) A. Z. Borucka, J. O'M. Bockris, and J. A. Kitchener, *ibid.*, **A241**, 554 (1957).

ties between these models such that they resemble one another more and more.¹⁵

The purpose of this paper is to present results of isothermal measurements of the conductance of fused NaNO_3 , in conjunction with solubilities of He and Ar in this melt, under various saturating pressures of these gases. An explanation of the results is advanced in terms of dilution effects being different for the gases, and the possible occupancy of liquid free volume as holes by a part of the dissolved gas solute. The first such measurement, using a single saturating pressure of Ar, has already been communicated.¹⁶

Experimental Section

Materials. Reagent grade NaNO_3 from Baker and Adamson and from Fisher was employed in the Ar solubility determinations. The Baker and Adamson salt was used without purification other than drying. The Fisher chemical was also dried, but exhibited traces of a residue which was insoluble in the fused salt. The residue eventually settled, and the pure molten salt was then decanted. Only the Baker and Adamson salt was used for all conductance and He solubility determinations. Argon and helium were from the National Cylinder Gas Co., and each had a stated purity of better than 99.99%.

Apparatus. A 500-ml. capacity Inconel metal bomb, Type A243HC5 of the Parr Instrument Co., was fitted with two CONAX thermocouple glands packed with "Lava" (a natural magnesium silicate). Each of these glands contained a chromel-alumel thermocouple during the solubility determinations. One such thermocouple junction was positioned centrally in the lower half of the bomb (within the fused salt), and the other junction was located similarly in the upper half of the system (within the gas phase). For conductance measurements the upper thermocouple was replaced by two 20-gauge platinum wire electrodes which extended down to the same level as the lower thermocouple junction. These platinum wires were sealed in 3.5-mm. o.d. Pyrex tubes such that only about the lower 7-mm. length of each wire was exposed to the liquid salt. Thermocouples were protected against corrosion by sealed thin-wall Pyrex tubes. The precalibrated thermocouples were accurate to better than $\pm 0.5^\circ$ over the ranges employed. The bomb was further equipped with a 0-8000-p.s.i.g. Supergauge manufactured by the U. S. Gauge Division of Ametek. The accuracy of this gauge, as quoted by the manufacturer, was ± 40 p.s.i., or slightly better than ± 3 atm. The bomb was sealed with a heavy-duty copper gasket.

An Aminco air-operated, single-ended diaphragm-

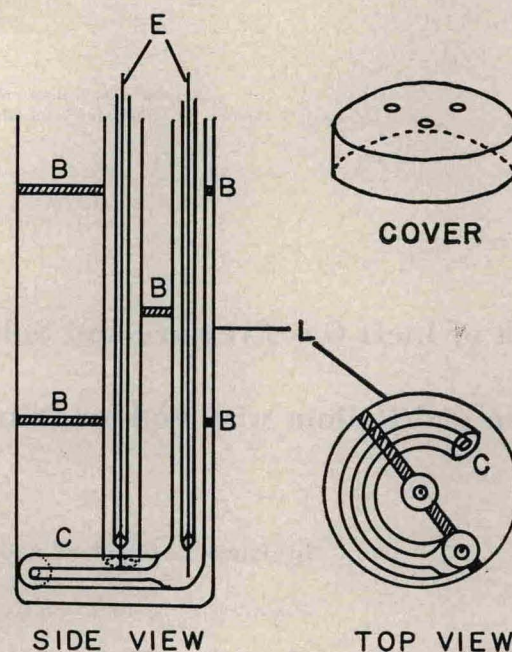


Figure 1. Capillary liner-cell for containing fused NaNO_3 and measuring its conductance under inert gas pressure. Legend: B, solid Pyrex braces; C, capillary; E, electrodes (Pt) in tubes; L, liner. All parts are of Pyrex except the Pt wires.

type compressor, No. 46-4025, was used for charging the bomb if a gas pressure greater than that in the cylinder was required. This booster pump has the advantage that the gas comes in contact only with clean, dry metallic surfaces with no trace of lubricant. A Cenco No. 91105-1 Hyvac vacuum pump was used whenever complete evacuation of gas from the bomb was desired.

Electrical resistance of the salt was measured directly using a Leeds and Northrup No. 4760 a.c.-d.c. Wheatstone bridge, with a No. 2370 60-cycle a.c. galvanometer. All leads were of shielded cable, and the bridge

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