

circuit was isolated from electrical ground. The body of the bomb was grounded, which made it serve as a natural electrical shield for the conductance cell and electrodes within. Sensitivity of the bridge arrangement was  $\pm 0.1$  ohm with typical resistance readings being in the 200–300-ohm range.

A Pyrex capillary conductance cell was integral to a 15-cm. deep Pyrex liner constructed from 6-cm. o.d. tubing sealed flat on the bottom. This liner-cell, with electrodes in position, is shown in Figure 1. The arc of the capillary lay in a horizontal plane common to the lower thermocouple junction and the platinum electrodes. This ensured temperature uniformity at the observed value throughout the conduction path. The cell constant was about 350  $\text{cm.}^{-1}$ .

A large 10-cm. i.d. vertical electrical furnace was used for heating the bomb assembly to the desired temperature.

**Procedures.** The determination of the solubility of Ar in fused  $\text{NaNO}_3$  has already been described.<sup>17</sup> The He solubility determinations were performed in like manner. However, detailed  $P$ - $\bar{V}$ - $T$  data for He over the desired ranges were not available. Therefore, the data of Holley, Worlton, and Zeigler<sup>18</sup> were used as the basis for computing solutions to the Beattie-Bridgeman equation, with an IBM 1410 computer, for the molar volumes of He under the prevailing conditions.

The conductance of a simple fused salt generally changes rapidly in the vicinity of the melting point due to remnants of the solid crystal lattice. Therefore, care must be taken to make measurements at sufficiently high temperatures.<sup>19–21</sup> Bloom and Heymann suggest safe lower temperature limits of 10% above the melting point, in degrees absolute.<sup>19</sup> Thus, the lower temperature limit for conductance measurements of  $\text{NaNO}_3$  (m.p.  $\sim 580^\circ\text{K.}$ ) should be about  $638^\circ\text{K.}$  ( $365^\circ$ ). This temperature is also low enough to preclude decomposition of the salt. The actual salt temperature at which conductance and solubility data were taken was  $369^\circ$ . To determine the conductance of  $\text{NaNO}_3$  under various saturating pressures of Ar or He, the following procedure was employed. About 350 to 450 g. of dry, powdered  $\text{NaNO}_3$  was placed in a Pyrex liner-cell, which was subsequently sealed into the bomb. Air was evacuated from the system, and Ar or He was admitted into the unit at room temperature to some desired pressure. The bomb was then heated to a salt temperature of  $369^\circ$ , and resistance readings were taken after the temperature and pressure were constant within the sensitivities of the instruments employed. Increments of gas were periodically exhausted from the bomb, and new resistance meas-

urements were made after constancy was attained at each new (lower) pressure at the same temperature of  $369^\circ$ . This process was repeated until the last possible amount of gas was pumped out by the vacuum pump. Gas was then readmitted into the bomb in increasing increments to obtain new resistance readings for testing reproducibility. Stable resistance values were ensured at every pressure by frequent agitation of the system to preclude gas supersaturation of the melt and other possible metastable effects. Each over-all conductance experiment was performed over a minimum interval of 48 hr.

## Results

Detailed results of the Ar solubility determinations have already been reported.<sup>17</sup> Henry's law constant for this solubility at  $369^\circ$ ,  $K_{\text{Ar}}$ , over an experimental range from 70 to 451 atm., was found to be

$$K_{\text{Ar}} = (17.2 \pm 1.7) \times 10^{-7} \text{ mole cm.}^{-3} \text{ atm.}^{-1} \quad (1)$$

The error is the probable error for a single result.

The He solubility data for  $\text{NaNO}_3$  at  $369^\circ$  are summarized in Table I and are plotted in Figure 2. Henry's law constant,  $K_{\text{He}}$ , over an experimental pressure range from 110 to 321 atm., is

$$K_{\text{He}} = (22.7 \pm 0.7) \times 10^{-7} \text{ mole cm.}^{-3} \text{ atm.}^{-1} \quad (2)$$

where the error is the probable error for a single result.

**Table I:** Saturation Concentration of He,  $C_{\text{He}}$ , at  $369^\circ$  in Molten  $\text{NaNO}_3$  at He Pressures,  $P_{\text{He}}$

$P_{\text{He}}$ , atm.	110	138	197	243	321
$C_{\text{He}} \times 10^4$ , mole $\text{cm.}^{-3}$	2.65	3.94 <sup>a</sup>	4.44	5.48	7.17

<sup>a</sup> Eliminated from statistical analysis according to Chauvenet's principle.

Tables II and III list the specific and equivalent conductance data in the order obtained for  $\text{NaNO}_3$  under various saturating pressures of Ar and He, respectively. The densities of gas-saturated liquid

(17) J. L. Copeland and W. C. Zybko, *J. Phys. Chem.*, **69**, 3631 (1965).

(18) C. E. Holley, Jr., W. J. Worlton, and R. K. Zeigler, "Compressibility Factors and Fugacity Coefficients Calculated from the Beattie-Bridgeman Equation of State for Hydrogen, Nitrogen, Oxygen, Carbon Dioxide, Ammonia, Methane, and Helium," Los Alamos Scientific Laboratory of the University of California, Los Alamos, N. M., Project LA-2271, 1959.

(19) H. Bloom and E. Heymann, *Proc. Roy. Soc. (London)*, **A188**, 392 (1947).

(20) E. R. Van Artsdalen and I. S. Yaffe, *J. Phys. Chem.*, **59**, 118 (1955).

(21) I. S. Yaffe and E. R. Van Artsdalen, *ibid.*, **60**, 1125 (1956).



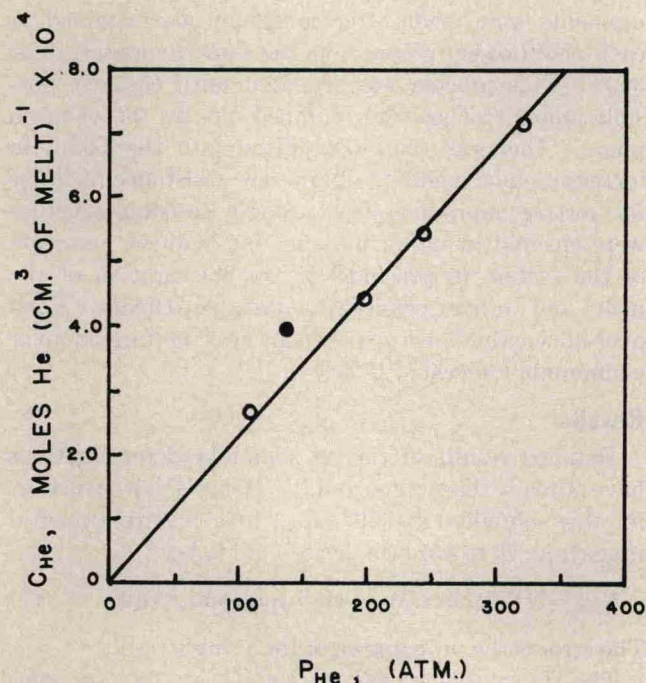


Figure 2. Solubility of helium in molten  $\text{NaNO}_3$  at  $369^\circ$ ,  $C_{\text{He}}$ , vs. saturating pressure of helium,  $P_{\text{He}}$ . Solid point has been disregarded in statistical analysis according to Chauvenet's principle.

$\text{NaNO}_3$  at  $369^\circ$ , used to calculate equivalent conductance, were obtained from the equation

$$d_{\text{NaNO}_3} = 1.875 + (3.9 \times 10^{-5})P \text{ g. cm.}^{-3} \quad (3)$$

which was deduced from density-piston pressure data (in the absence of a gas phase) of Owens.<sup>22</sup> Figure 3 shows that, empirically, the specific conductance varies linearly with saturating pressure of either gas in the pressure ranges studied. A linear relationship also exists for the equivalent conductance. However, values of the latter quantity are not as accurate as those of the specific conductance since it was not possible to measure accurately the volume of the gas-saturated salt. In view of the relatively weak interactions between solvent and solute particles, a quantity of dissolved inert gas should tend to augment the equivalent volume of the salt, unless the solute molecules take up liquid free volume principally. Hence, use of the tabulated densities of  $\text{NaNO}_3$  under ordinary piston pressure probably yield values of equivalent conductance which are too low by several per cent at the higher pressures, but which are more and more accurate for the lower gas concentrations. Least-squares analyses yield the following empirical equations for conductances of  $\text{NaNO}_3$  at  $369^\circ$  as functions of saturating pressure of Ar or He in atmospheres.

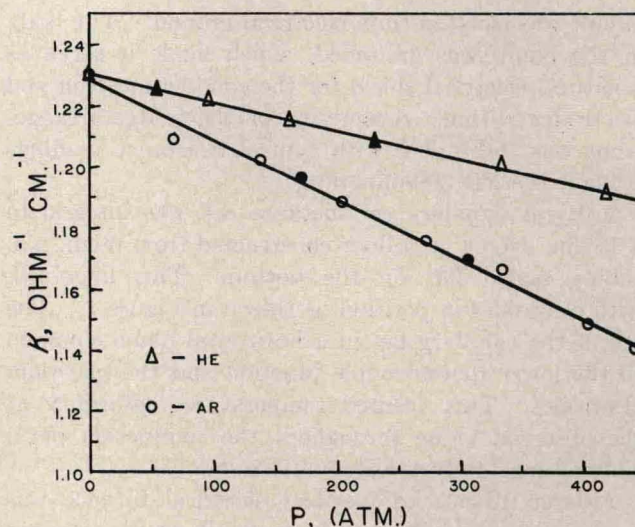


Figure 3. Specific conductance of molten  $\text{NaNO}_3$  at  $369^\circ$  under helium or argon pressure. Open points denote decreasing pressures; solid points denote increasing pressures.

Table II: Summary of Specific Conductance and Equivalent Conductance of  $\text{NaNO}_3$  at  $369^\circ$  under Ar Pressure

Saturating pressure, $P_{\text{Ar}}$ , atm.	Specific conductance, $\kappa_{\text{Ar}}$ , $\text{ohm}^{-1} \text{ cm.}^{-1}$	Density, <sup>a</sup> $d_{\text{NaNO}_3}$ , $\text{g. cm.}^{-3}$	Equiv. conductance, $\Lambda_{\text{Ar}}$ , $\text{cm.}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1}$
443	1.140	1.892	51.20
404	1.148	1.891	51.61
334	1.166	1.888	52.49
272	1.175	1.886	52.96
204	1.188	1.883	53.62
138	1.202	1.880	54.33
68	1.209	1.878	54.72
0	1.230 <sup>b</sup>	1.875	55.75
172	1.196	1.882	54.02
307	1.169	1.887	52.65

<sup>a</sup> Density values are for the pure liquid salt under piston pressure only. <sup>b</sup> This value, interpolated from published data of Klemm, gave the cell constant  $368.1 \text{ cm.}^{-1}$  (A. Klemm in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, New York, N. Y., 1964, Chapter on "Transport Properties of Molten Salts").

For Ar

$$\kappa_{\text{Ar}} = (1.228 \pm 0.002) -$$

$$(1.94 \pm 0.06) \times 10^{-4} P_{\text{Ar}} \text{ ohm}^{-1} \text{ cm.}^{-1} \quad (4a)$$

$$\Lambda_{\text{Ar}} = 55.65 - 9.86 \times 10^{-3} P_{\text{Ar}}$$

$$\text{cm.}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1} \quad (4b)$$

(22) B. B. Owens, private communication to J. L. C., 1965.