

[Reprinted from the Journal of the American Chemical Society, 86, 4734 (1964).]
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Effect of Inert Gas Pressure and Solubility on Electrical Conductance in Fused Salts

Sir:

We wish to present a preliminary report on recent data resulting from a study of the mechanism of electrical conductance in pure fused salts.

A 500-ml. capacity Inconel metal bomb, Type A24-3HC5 of the Parr Instrument Co., was fitted with two CONAX thermocouple glands packed with a natural magnesium silicate. One of these glands contains a Chromel-Alumel thermocouple, and the other contains a pair of 20-gauge platinum wires for conductance electrodes. Pyrex bomb liners were prepared with capillary conductance cells fixed rigidly within them. In a typical experiment, such a liner-cell is charged with about 450 g. of dry NaNO_3 weighed to the nearest 0.5 g. Argon is admitted at room temperature into the sealed, evacuated bomb, containing the liner-cell and its salt charge, to a desired pressure. The number of moles of Ar introduced is calculated with the aid of the compressibility factor chart of Maslan and Littman¹ using the equilibrium values of pressure, room temperature, and the gas volume (known from the total volume of the bomb less the volumes of the liner-cell and its salt charge). The bomb is then heated in a furnace to a new temperature well above the melting point of NaNO_3 . Conductance measurements are made on the fused salt at equilibrium temperature and pressure. The number of moles of gaseous Ar still remaining is calculated from the new values of equilibrium temperature, pressure, and gas volume (the old volume corrected for change in density of the salt and its compression) with the aid of the same compressibility chart. Decrease in moles of gaseous Ar is attributed to its solubility in the melt, the latter then being calculated. The gas is slowly evacuated from the system, and the latter is pumped out to remove all Ar from the melt. New conductance readings are then taken on the gas-free melt at the same temperature.

First results for NaNO_3 , using a capillary conductance cell of about 184-cm.^{-1} cell constant, indicate a 5.7% decrease in specific conductance when the melt at 369° was subjected to 362 atm. of Ar. The conductance measurements showed excellent precision for both the gas-saturated and gas-free melt, yielding specific conductances of $1.16\text{ ohm}^{-1}\text{ cm.}^{-1}$ for the melt under pressure, and $1.23\text{ ohm}^{-1}\text{ cm.}^{-1}$ for the normal liquid, both at 369° . Maximum experimental error in these values is believed to be less than $\pm 0.01\text{ ohm}^{-1}\text{ cm.}^{-1}$. The Henry's law constant determined for the solubility of Ar in fused NaNO_3 under these conditions, based on two independent determinations, was 18.7×10^{-7} and 19.6×10^{-7} mole of Ar (cm.^3 of melt) $^{-1}$ atm. $^{-1}$.

We believe that the observed conductance decrease under pressure is due to loss of free volume available

for transport in the melt. In the hole theory of fused salts, the volume increase on melting, ΔV , is attributed almost entirely to holes.² For NaNO_3 this is 4.32 cm.^3 mole $^{-1}$, or a 10.7% volume increase.³ The isothermal compressibility coefficient, β_T , for fused NaNO_3 is about $20.4 \times 10^{-12}\text{ cm.}^2\text{ dyne}^{-1}$ at 370° , based on interpolation of the data of Bockris and Richards.⁴ Using these data in conjunction with a density of 1.87 g. cm.^{-3} for NaNO_3 at 369° ,⁵ we arrive at an approximate upper limit loss of holes of about 8.8% due to compression by 362 atm. of Ar alone. Thus, if hole density is the major factor controlling conductance of a pure fused salt,⁶ we would expect an approximate upper limit conductance decrease of fused NaNO_3 of 8.8% under these conditions owing to compression alone. This is not irreconcilable with our observed 5.7% decrease. On the other hand, the theoretical molar density of holes in a pure fused salt is given as⁴

$$N_H = (\Delta V/0.68)(\gamma/kT)^{3/2}$$

where γ is the liquid-vapor surface tension, k is Boltzmann's constant, and T is the absolute temperature. Using this equation with a value of $\gamma = 113.5\text{ dynes cm.}^{-1}$ at 369° ,⁷ in conjunction with the density of NaNO_3 , the volume density of holes is 4.86×10^{21} holes cm.^{-3} . Our average Henry's law constant together with this figure reveals that if Ar atoms dissolve by occupying existing holes, about 8.6% of the holes would be occupied and thereby removed from the conductance mechanism. This value is also not at odds with the observed conductance decrease. Considered separately, the theoretical conductance decrease due to either compression of the melt or gas solubility alone is in line with observation. There can be no doubt that free volume is reduced by compression of the melt, but it may be doubtful if inert gas molecules dissolve by occupying existing holes. The positive enthalpies of solution observed by Grimes, Smith, and Watson⁸ may well indicate that solution occurs by the molecules creating their own holes, leaving most of the original holes intact. We therefore believe that loss of holes by compression may possibly be the major factor in the resulting diminution of conductance. Studies are being undertaken using other inert gases at the same pressure and temperature to ascertain if there is any dependence of conductance change on solubility.

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RECEIVED SEPTEMBER 18, 1964