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Effect of Inert Gas Pressure and Solubility on Fused Salt Conductance. I. Argon and Helium with Sodium Nitrate[1]

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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 $K_{Ar} = (17.2 \pm 1.7) \times 10^{-7}$ mole of Ar (cm.^{3} of melt)$^{-1}$ atm.$^{-1}$ and $K_{He} = (22.7 \pm 0.7) \times 10^{-7}$ 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: $\kappa_{Ar} = (1.228 \pm 0.002) - (1.94 \pm 0.06) \times 10^{-4}P_{Ar}$ ohm^{-1} cm.$^{-1}$; and, for He: $\kappa_{He} = (1.230 \pm 0.001) - (9.19 \pm 0.25) \times 10^{-5}P_{He}$ 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 Altar[3] 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-

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[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 ±0.5° 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.

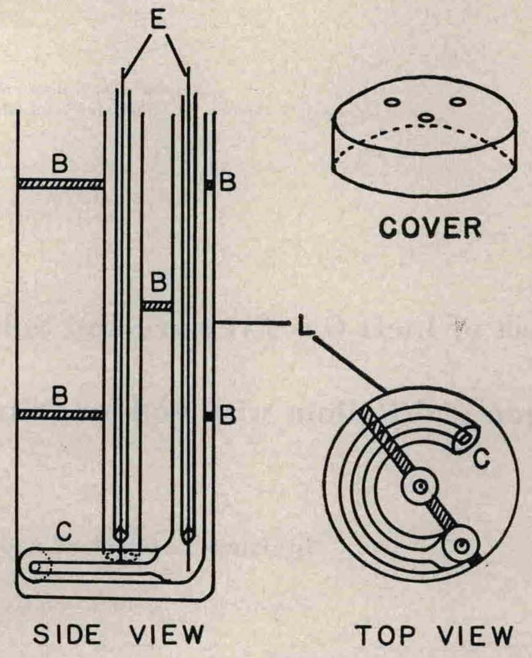

Figure 1. Capillary liner–cell for containing fused $NaNO_3$ and measuring its conductance under inert gas pressure. Legend: B, solid Pyrex braces; C, capillary; E, electrodes (Pt) in tubes; L, liner. All parts are of Pyrex except the Pt wires.

An Aminco air-operated, single-ended diaphragm-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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(7) J. O'M. Bockris and G. W. Hooper, *Discussions Faraday Soc.*, **32**, 218 (1961).

(8) S. B. Tricklebank, L. Nanis, and J. O'M. Bockris, *J. Phys. Chem.*, **68**, 58 (1964).

(9) J. O'M. Bockris, S. Yoshikawa, and S. R. Richards, *ibid.*, **68**, 1838 (1964).

(10) M. K. Nagarajan, L. Nanis, and J. O'M. Bockris, *ibid.*, **68**, 2726 (1964).

(11) J. O'M. Bockris, S. R. Richards, and L. Nanis, *ibid.*, **69**, 1627 (1965).

(12) C. A. Angell, *ibid.*, **68**, 218 (1964).

(13) C. A. Angell, *ibid.*, **68**, 1917 (1964).

(14) C. A. Angell, *ibid.*, **69**, 399 (1965).

(15) H. Bloom and J. O'M. Bockris in "Fused Salts," B. R. Sundheim, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964, Chapter 1.

(16) J. L. Copeland and W. C. Zybko, *J. Am. Chem. Soc.*, **86**, 4734 (1964).

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 ±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 $cm.^{-1}$.

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 $NaNO_3$ has already been described.[17] 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[18] 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.[19–21] Bloom and Heymann suggest safe lower temperature limits of 10% above the melting point, in degrees absolute.[19] Thus, the lower temperature limit for conductance measurements of $NaNO_3$ (m.p. ~580°K.) should be about 638°K. (365°). 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°. To determine the conductance of $NaNO_3$ under various saturating pressures of Ar or He, the following procedure was employed. About 350 to 450 g. of dry, powdered $NaNO_3$ 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°, 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 measurements were made after constancy was attained at each new (lower) pressure at the same temperature of 369°. 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.[17] Henry's law constant for this solubility at 369°, K_{Ar}, over an experimental range from 70 to 451 atm., was found to be

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

The error is the probable error for a single result.

The He solubility data for $NaNO_3$ at 369° are summarized in Table I and are plotted in Figure 2. Henry's law constant, K_{He}, over an experimental pressure range from 110 to 321 atm., is

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

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

Table I: Saturation Concentration of He, C_{He}, at 369° in Molten $NaNO_3$ at He Pressures, P_{He}

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

[a] 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 $NaNO_3$ under various saturating pressures of Ar and He, respectively. The densities of gas-saturated liquid

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(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).

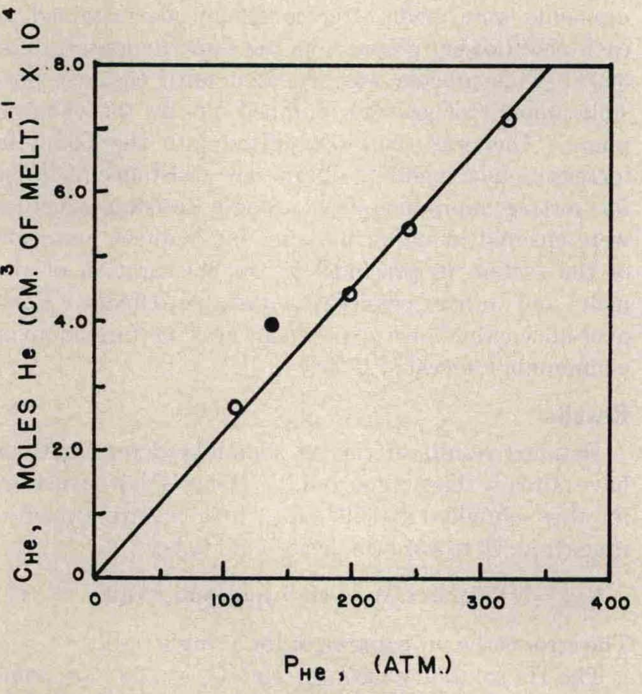

Figure 2. Solubility of helium in molten $NaNO_3$ at 369°, C_{He}, *vs.* saturating pressure of helium, P_{He}. Solid point has been disregarded in statistical analysis according to Chauvenet's principle.

$NaNO_3$ at 369°, used to calculate equivalent conductance, were obtained from the equation

$$d_{NaNO_3} = 1.875 + (3.9 \times 10^{-5})P \text{ g. cm.}^{-3} \quad (3)$$

which was deduced from density–piston pressure data (in the absence of a gas phase) of Owens.[22] 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 $NaNO_3$ 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 $NaNO_3$ at 369° as functions of saturating pressure of Ar or He in atmospheres.

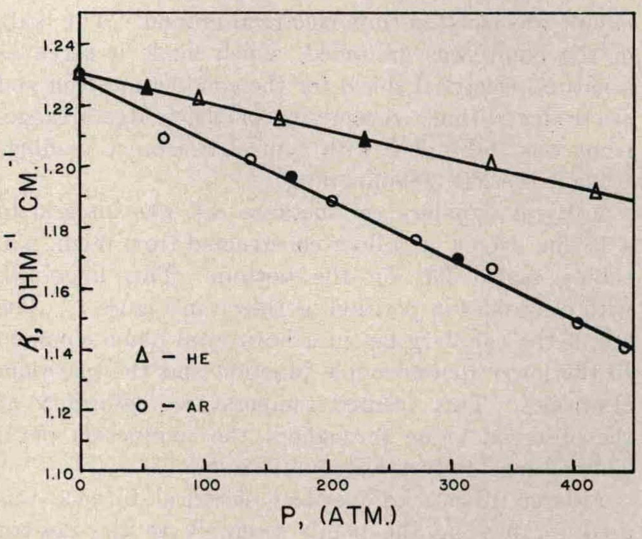

Figure 3. Specific conductance of molten $NaNO_3$ at 369° under helium or argon pressure. Open points denote decreasing pressures; solid points denote increasing pressures.

Table II: Summary of Specific Conductance and Equivalent Conductance of $NaNO_3$ at 369° under Ar Pressure

Saturating pressure, P_{Ar}, atm.	Specific conductance, κ_{Ar}, ohm^{-1} cm.$^{-1}$	Density,[a] d_{NaNO_3}, g. cm.$^{-3}$	Equiv. conductance, Λ_{Ar}, cm.^{2} ohm^{-1} 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[b]	1.875	55.75
172	1.196	1.882	54.02
307	1.169	1.887	52.65

[a] Density values are for the pure liquid salt under piston pressure only. [b] This value, interpolated from published data of Klemm, gave the cell constant 368.1 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

$$\kappa_{Ar} = (1.228 \pm 0.002) - (1.94 \pm 0.06) \times 10^{-4} P_{Ar} \text{ ohm}^{-1} \text{ cm.}^{-1} \quad (4a)$$

$$\Lambda_{Ar} = 55.65 - 9.86 \times 10^{-3} P_{Ar} \text{ cm.}^2 \text{ ohm}^{-1} \text{ equiv.}^{-1} \quad (4b)$$

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

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}, ohm^{-1} cm.$^{-1}$	Density,[a] d_{NaNO_3}, g. cm.$^{-3}$	Equiv. conductance, Λ_{He}, cm.^{2} ohm^{-1} 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

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

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

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 as[24]

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

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 Å., and that of Ar is 1.92 Å.,[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 Å., that of NO_3^- is 2.3 Å.[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

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(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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