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The Influence of Water on the Mechanical Properties of a Glass-Epoxy Matrix Composite

M. R. Stoudt, E. Escalante and R. E. Ricker

Corrosion Group

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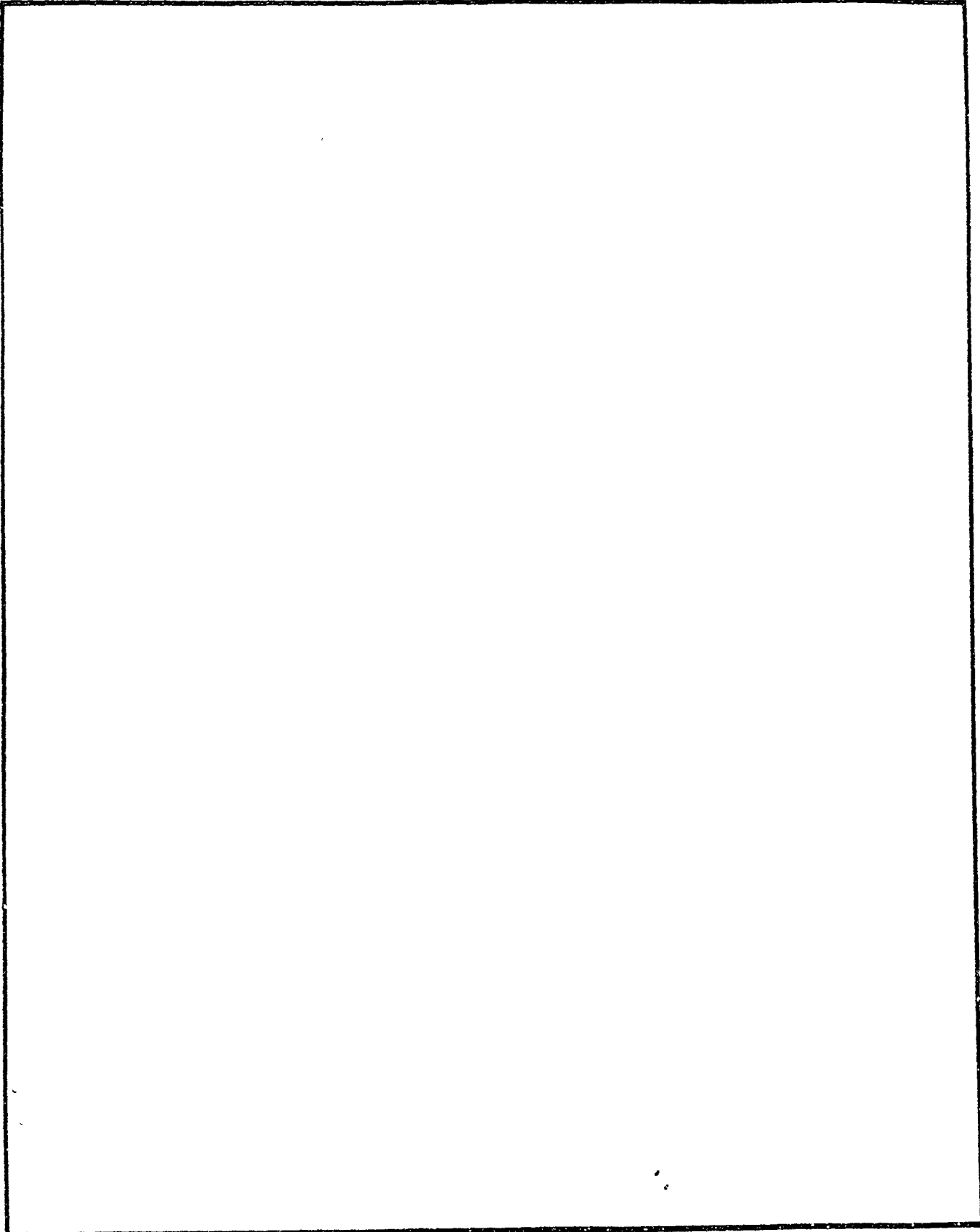
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THE INFLUENCE OF WATER ON THE MECHANICAL PROPERTIES OF A GLASS-EPOXY MATRIX COMPOSITE

M. R. Stoudt, E. Escalante and R. E. Ricker
Corrosion Group, Material Science and Engineering Laboratory, National
Institute of Standards and Technology, Gaithersburg, MD 20899

ABSTRACT

The influence of exposure to water at ambient pressure and at an elevated pressure on the mechanical properties of a glass fiber epoxy matrix composite was investigated. The mechanical properties of three orientations of the composite were determined in the dry condition, after exposure to water at ambient pressure and after exposure to water at 5.9 MPa. Then, to determine the mechanism of the observed degradation, the mechanical properties of samples exposed at the two pressures were determined after the absorbed water was removed. The rate and extent of water absorption and desorption was evaluated by measuring the weight change at periodic intervals.

Substantial reductions in the yield stress and the ultimate strength were observed for samples at both pressures. On desorption, the yield stress returned to the originally determined dry value, but the ultimate strength was not recovered. This was attributed to a permanent degradation of the glass fibers by the absorbed water. No significant difference was observed for samples exposed at the two pressures.

INTRODUCTION

Polymer matrix composite materials (PMC's) exhibit good mechanical properties and resistance to aggressive environments. Because of these and other properties, PMC's are utilized in a variety of marine applications and are under consideration for more demanding applications such as deep water submersibles. The ability of these materials to perform under extreme pressure conditions has been the subject of research, but many uncertainties still remain as to what effects absorbed water may have on the mechanical properties of a PMC and whether or not these effects are aggravated by pressure.

Absorbed water has a plasticizing effect on polymers which generally results in a significant reduction in the yield strength and it has been demonstrated that absorbed water has a similar effect on PMC's.^{1,2} It has been postulated that water penetrates into a PMC by two basic processes: diffusion through the resin phase, and by transport through defects such as cracks and holes.¹ It is also

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thought that the interface between the fiber and the matrix plays an important role in the absorption of water because of the capillary-like nature of this region.^{1,2} Since research has shown that room temperature saturation of a PMC is reached at least one order of magnitude more rapidly than saturation of the polymer matrix alone^{1,2} and that diffusion is not directly effected by changes in pressure,^{2,3,4} it is now generally believed that the primary mechanism of water absorption in these materials is the permeation of water through the region of the fiber/matrix interface and defects, not bulk diffusion through the matrix. Based on this, it can be hypothesized that an increase in the exposed fiber-matrix interfacial area would increase the rate of absorption of water by a PMC.^{1,5} It has also been suggested that high pressure could increase this transport of water significantly accelerating the overall water uptake of the composite.⁶

It is generally accepted that, water present in the matrix of a PMC will induce a reduction in the mechanical strength of the PMC.^{1,2,3,5} This reduction in strength has been attributed to a combination of several effects related to the components of the composite some of which will be reversible and others irreversible. Effects such as a decrease in the glass transition temperature of the resin, and an increase in internal stresses resulting from swelling of the matrix are basically physical changes and will be reversible on desorption of the absorbed water. Chemical changes resulting from degradation reactions between the absorbed water and individual components of the composite will induce permanent damage.^{2,4}

In 1989, Tucker and Brown⁶ reported the results of experiments on a PMC exposed to seawater at two different pressures. They reported that exposure at a pressure equivalent to a 2000 foot submersion (5.9 MPa) resulted in an increase in the water absorbed as compared to exposure at atmospheric pressure. This increase in water absorption resulted in a greater reduction in the mechanical properties, but no significant difference in the diffusion coefficient was found. Based on the assumption that vapor pressure is relatively unaffected by pressure over the range examined, Tucker and Brown⁶ concluded that this increase in the water absorbed must be due to an increase in the residence sites for water in the composite resulting from damage caused by the high pressure. Since no evidence of blistering was found, they concluded that increased osmotic pressure and blister growth could not be the cause of this pressure effect and that "mechanical damage to preexisting voids and defects in the composite" must be responsible for the increased water uptake and strength decrease at the higher pressure.⁶

The mechanism that Tucker and Brown⁶ concluded was responsible for the degradation that they observed should not be limited to the system that they studied. That is, permanent mechanical damage to preexisting voids as a result of exposure to high pressure water could occur in other PMC systems such as glass fiber reinforced composites which are commonly used in marine applications and are under consideration for applications that require exposure to high pressure sea water. As a result, the hypothesis that this mechanism would cause a degradation in the properties of a glass fiber reinforced composite was evaluated by exposing samples to water at ambient pressure and at an elevated pressure. Since numerous authors have found that pure water is as damaging as

salt water to these types of composites, distilled water was used for these experiments rather than salt water or sea water.⁷⁻⁹ To allow distinction between permanent damage mechanisms and degradation mechanisms that require water to be present during loading, this experimental program included experiments on samples which were dried to remove the absorbed water after the exposures at the two pressures.

EXPERIMENTAL

The material selected for this study was a commercially produced, E-glass (borosilicate) fiber cloth reinforced, epoxy matrix composite (manufacturer designation, G-10). This was chosen primarily because the mechanical properties and the water absorption characteristics of this material have been well characterized (ASTM D-709). Samples were cut from sheet stock consistent with ASTM Standard D-790 in the orientations designated as 0°, 90° and 45° with respect to the warp or primary fiber direction of the cloth (the secondary fiber direction, the woof, is perpendicular to the warp). To ensure a fully dry initial condition, the samples were stored in a desiccator at ambient pressure for six months prior to testing. To characterize the initial, fully dry, properties, samples were tested in four-point bend in lab air on a screw-type tensile machine with the load and displacement data recorded by computer. Then, the remaining samples were immersed in distilled water at ambient pressure and at a pressure of 5.9 MPa. The samples were removed periodically during this exposure, dried to remove excess surface moisture, and weighed. After an exposure period of approximately 70 days, half of the remaining samples were removed and tested in four point bend while the other half were placed in a desiccator to remove the absorbed water. The weight of the samples was measured periodically during the desorption process and after the weight returned to the initial value, the mechanical properties of these samples were determined in the same manner as before. The fracture surfaces were sputter coated with gold prior to examination in a scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Figure 1 shows the percentage of weight gained as a result of water absorption as a function of exposure time for the samples exposed to pure water at 5.9 MPa. The water absorption curve at ambient pressure is essentially identical to this curve. In this figure, it can be seen that, except for small statistical deviations, the 0° and the 90° orientations exhibited identical behavior. The 45° orientation deviated slightly from this behavior and, in figure 1, it can be seen that this orientation exhibited greater weight gains at each measurement. Figure 2 compares the behavior of the samples cut in the 45° orientation at the two pressures. No effect of pressure on the absorption of water is indicated and similar behavior was observed for the other orientations. Therefore, pressure had no effect on the water absorption characteristics and the deviation between the 45° orientation and the other orientations is believed to be a result of either an increase in the solubility of water or an increase in the rate of transport of water

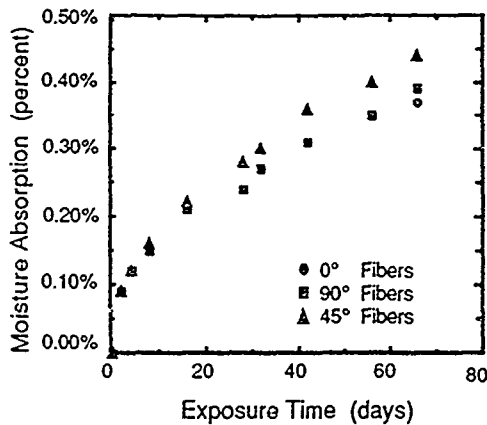


Figure 1 Weight Gain vs Time Curve for G-10 at 5.9 MPa Pressure

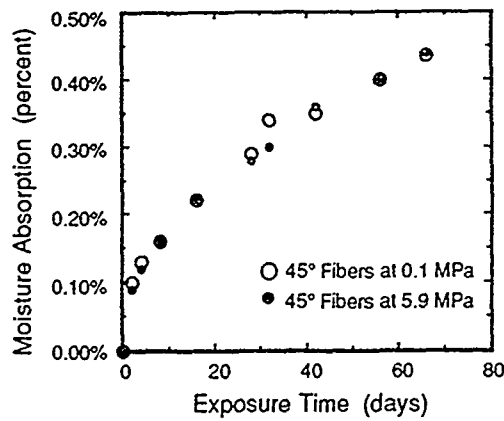


Figure 2 Weight Gain vs Time Curve for 45° Orientation at 0.1 MPa and 5.9 MPa Pressure.

into the composite as a result of the increased fiber-to-matrix interface exposed to the solution for this orientation.

The data given in Table I are the results of the mechanical tests. Each value in the table corresponds to a mean value and the standard deviation for three individual experiments except for those values denoted with an asterisk (*) which represent singular data points. As expected, absorption of water by the composite resulted in a reduction of the mechanical properties for all three sample orientations and this effect is clearly demonstrated in the yield stress data (determined by the 0.2% offset method). In the fully dry condition, the composite possessed yield stresses of 296 MPa and 321 MPa for the 0° and the 90° orientations respectively, while in the saturated condition, the yield stress was reduced to 227 MPa (approximately 25%) for the 0° orientation and to 269 MPa (approximately 20%) for the 90° orientation. There was no significant difference in the extent of this reduction in the yield strength for the samples exposed to water at the two different pressures (approximately 15% for both 0° and 90°). This indicates that the increased pressure had no significant influence on the mechanical properties.

If the influence of absorbed water on the mechanical properties of the composite is due only to the plasticizing effects of water on the polymer matrix, then all of the mechanical properties would be restored upon desorption of the absorbed water. As shown in Table I, the yield stress did regain essentially all of the original magnitude after a drying period of two hundred days (approximately 96% and 100% for the 0° and for the 90° orientations respectively). However, the ultimate strength continued to decline for both the ambient and the elevated pressure exposures indicating that permanent damage may be present in the composite. One explanation for this behavior might be that the decline in the ultimate strength resulted from a degradation reaction which occurred between the glass reinforcing fibers and the water present in the matrix, but additional examinations will be required to evaluate the cause and the permanence of the decline.

Table 1. The Influence of Absorbed Water on the Mechanical Properties

Testing Condition	Fiber Orientation	Ultimate Strength MPa	$\sigma_{(n-1)}$	Yield Stress MPa	$\sigma_{(n-1)}$
<i>Fully Dry</i>	0°	353	13	296	10
	90°	406	1	321	5
	45°	276	10	164	6
<i>Saturated at 0.1 MPa</i>	0°	342	8	227	9
	90°	380	5	269	8
	45°	253	3	102	7
<i>Saturated at 5.9 MPa</i>	0°	344	5	252	9
	90°	386	2	270	6
	45°	256	4	107	9
<i>Saturated at 0.1 MPa</i>	0°	323*	n/a	283*	n/a
	90°	388*	n/a	335*	n/a
	45°	174*	n/a	155*	n/a
<i>Saturated at 5.9 MPa</i> <i>Desorbed 200 Days</i>	0°	333	8	291	14
	90°	381	1	334	6
	45°	182	1	160	8

In order to achieve the maximum strength from a polymer composite material, it is essential to have good bonding between the fiber and the matrix since this is where load is transferred between the matrix and the fibers. Figure 3 shows a fiber bundle which was exposed on the fracture surface of a sample tested in the initial dry condition. A substantial amount of matrix can be seen clinging to the surfaces of the fibers which indicates good fiber-matrix interface adhesion. The fracture surfaces generated with absorbed water present were similar to the dry fracture surfaces though slightly more ductile, Figure 4. The fracture surfaces of the desorbed samples were indistinguishable from those of the initial dry condition as shown in Figure 5. In this figure, two fibers partially pulled from the matrix possess a large amount of clinging matrix material indicating good fiber-matrix adhesion.

Based on these results, it can be said that the absorbed water had some effect on each component of the glass-epoxy composite, but the effect was shown to be independent of pressure since there was no significant difference in the mechanical properties between the two pressures. While the effect of moisture on the bond between the matrix and the fibers was essentially reversible, permanent damage to the fibers themselves may be the cause of the irreversible decrease in the ultimate strength. Additional examinations will be required to determine the exact nature of this decrease in the ultimate strength of the composite.

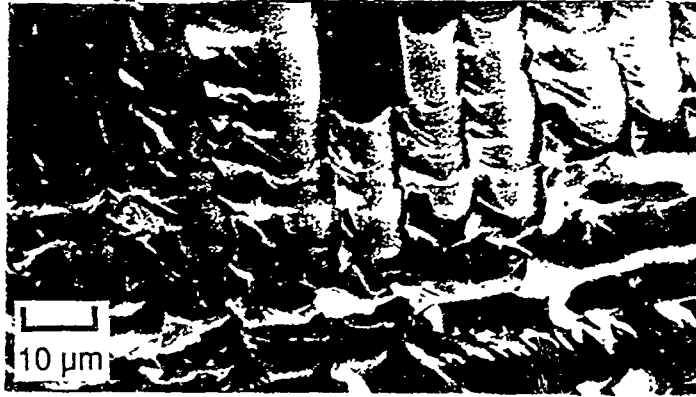


Figure 3 SEM Micrograph of a Fiber-Matrix Interface in the Fully Dry Condition



Figure 4 SEM Micrograph of a Fiber-Matrix Interface in the Saturated Condition

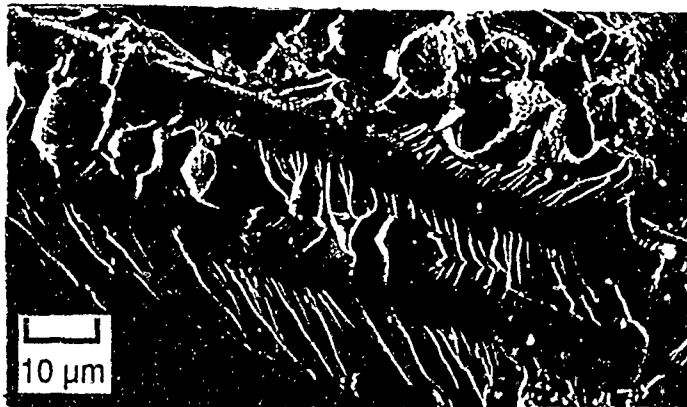


Figure 5 SEM Micrograph of a Fiber Pulled From the Matrix in the Desorbed Condition

CONCLUSIONS

The effects of water absorption and pressure on the mechanical properties of a glass fiber reinforced epoxy matrix composite were evaluated. The composite was exposed to pure water at both ambient and elevated pressures and an increase was observed in the water absorption in the 45° orientation as compared to the 0° and the 90° samples. This was attributed to either an increase in the solubility of water or an increase in the rate of mass transport as a result of the increase in the fiber-to-matrix interface exposed to the solution for this orientation. Pressure had no effect on the absorption of water by the composite.

When tested in four point bend in the water saturated condition, the composite exhibited a significant reduction in the yield stress and ultimate strength with respect to the fully dry condition. The difference in the values as a function of pressure was insignificant. Therefore, it was determined that the pressure had no influence on the degradation of the mechanical properties. Upon desorption, the composite demonstrated essentially complete restoration of the yield stress, but the ultimate strength continued to decrease indicating that an interaction occurred between the absorbed water and some component of the composite resulting in permanent damage. This is thought to be due to a degradation reaction between the glass fibers and the moisture present, but further analysis is planned to determine the exact nature of this effect.

The results of these experiments demonstrated that exposure to water at an elevated pressure had no influence on the water absorption characteristics and produced no significant change in the mechanical properties of a glass fiber epoxy matrix composite as compared to exposure at ambient pressure. More importantly, it was demonstrated that the effect of pressure observed by Tucker and Brown⁶ is not generic to all types of polymer matrix composites.

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R. Johnsen and R. Tosh

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L. A. Viehland

Parks College, Saint Louis University, Cahokia, Illinois 62206

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The mobility of helium ions in neon gas has been computed using an interaction potential inferred from spectroscopic data and the results are compared to values obtained by a drift-tube experiment. The computed values accurately reproduce the dependence of the mobility on E/n_0 at two temperatures, 77 and 300 K, thus supporting the potentials inferred from molecular spectroscopy.

I. INTRODUCTION

The traditional motivation for measuring ionic mobilities in dilute gases has been to obtain information about the interaction potentials between ions and neutrals. One procedure¹ for obtaining the potentials from measured transport data consists of assuming a parameterized form of the interaction potential, computing the ion mobility from approximate solutions of the Boltzmann equation (or from Monte Carlo calculations) and iteratively adjusting the potential parameters until good agreement is obtained between calculated and measured values. An alternative method for the direct determination of the interaction potential is also available.² The potentials obtained in either manner are generally as accurate as the best potentials obtained from *ab initio* calculations or extracted from other types of experiments, such as spectroscopy or beam scattering.

When interaction potentials are available from another source, gaseous ion mobilities can be used to assess their accuracy. Such a comparison is not very interesting when the interaction is adequately described by the long-range, ion-induced dipole (polarization) potential that varies as the inverse fourth power of the separation, since then the mobility is independent of both the gas temperature T_0 and the ratio E/n_0 of the electric field to the gas number density. However, gaseous ion mobilities generally exhibit pronounced dependences on T_0 and E/n_0 , reflecting a substantial deviation from the polarization potential. The striking mobility maxima that have been observed at certain values of E/n_0 in many ion-neutral systems reflect the transition from long-range collisions dominated by the attractive part of the potential to short-range collisions dominated by the repulsive wall. Correctly matching the dependence of the mobility on E/n_0 represents a severe test of a proposed interaction potential.

Accurate potentials are available for only a few ion-neutral systems. One of these is the interaction potential between He^+ ions and Ne atoms which is known as a result of the spectroscopic work of Dabrowski and Herzberg³ and the subsequent RKR fitting by Siska.⁴ The potential corresponds to an excited state of the HeNe^+ molecule, since the ionization potential of helium is larger than that of neon. In the present work, this potential was used to calculate the mobility of helium ions in neon gas at room temperature and at 77 K, these

mobilities were measured, and the accuracy of the potential was tested.

II. THEORETICAL CALCULATIONS

Siska's interaction potential for the $\text{He}^+ - \text{Ne}$ system is an MSV (Morse-spline-van der Waals) parametric equation. The β parameter of the Morse part of this interaction has the value 4.714, giving a well depth of 1.041 kcal/mol at the separation of 2.648 Å. The C_4 parameter describing the long-range van der Waals attraction has the value 65.64 Å⁴ kcal/mol, while the d parameter inserted to avert singular behavior at the origin has the value of 0.5 Å. The parameters for the spline portion of this potential were not explicitly given by Siska and had to be determined by numerically matching the logarithms and logarithmic derivatives of the spline with the Morse potential at a separation of 2.981 Å and with the van der Waals portion at 5.296 Å. We have found that these parameters are $b_0 = 1.86247$, $b_1 = -0.01198263$, $b_2 = -2.3139$, and $b_3 = 0.609204$.

We evaluated Siska's potential at 99 separations between 0.5 and 14.76 Å. This tabulated potential was then used as the input to program QVALULS⁵ which evaluated the first 30 transport cross sections to an accuracy of better than 0.2% at 49 energies ranging from 1×10^{-6} to 5 a.u. These cross sections were then used as input to program MOBDH1⁶ which solves the Boltzmann kinetic equation by a three-temperature approach.^{7,8} Good convergence was achieved for the mobilities and for the diffusion coefficients parallel and perpendicular to the electric field at all E/n_0 values when the gas temperature was T_0 was 295 K. At 77 K convergence was not good for E/n_0 values between 5 and 20 Td, where 1 Td = 10^{21} V m⁻². To determine the transport coefficients accurately in this E/n_0 range, we made use of the two-temperature computer program of Ness and Robson⁹ and bi-Maxwellian programs that have been developed recently.¹⁰ Our results are summarized in Tables I and II where the accuracy is limited to 0.2% by the accuracy of the cross sections. The tables include the computed values for the longitudinal and transverse diffusion coefficients expressed as products of the diffusion coefficients with gas density. The experiments only determined the mobilities.

TABLE I. Calculated transport coefficients for He⁺ in neon at 77 K.

E/n_0 (Td)	K_0 (cm ² /Vs)	$n_0 D_L$ (10 ¹⁹ /cm s)	$n_0 D_T$ (10 ¹⁹ /cm s)
0.168 94	13.64	0.243	0.243
0.548 54	13.64	0.244	0.244
0.988 20	13.65	0.248	0.246
2.001 12	13.67	0.262	0.256
3.199 41	13.72	0.293	0.277
4.035 89	13.79	0.326	0.299
5.000 00	13.98	0.391	0.336
7.000 00	14.51	0.618	0.459
8.000 00	14.88	0.799	0.555
10.0000	15.74	1.303	0.833
12.0000	16.6	1.91	1.225
14.0000	17.33	2.56	1.717
15.0000	17.58	2.86	1.98
16.0000	17.8	3.13	2.27
18.0000	18.13	3.66	2.85
20.0000	18.27	4.13	3.45
25.0000	18.16	5.16	4.98
30.0000	17.73	6.13	6.47
33.1333	17.46	6.7	7.42
38.6677	16.84	7.9	9.01
45.5085	16.14	9.4	10.9
53.5929	15.43	11.3	13.2
63.2083	14.73	13.6	16.0
74.5267	14.06	16.5	19.3
87.7987	13.43	19.7	23.0
103.261	12.86	24.2	27.9
121.178	12.32	28.8	34.2
141.802	11.85	35.8	41.7
165.394	11.44	44.7	51.2
192.190	11.09	56.0	63.0

TABLE II. Calculated transport coefficients for He⁺ in neon at 300 K.

E/n_0 (Td)	K_0 (cm ² /Vs)	$n_0 D_L$ (10 ¹⁹ /cm s)	$n_0 D_T$ (10 ¹⁹ /cm s)
0.277 95	16.61	1.16	1.15
0.500 25	16.62	1.16	1.16
1.012 63	16.63	1.17	1.16
2.044 16	16.7	1.21	1.19
3.253 20	16.83	1.29	1.24
4.085 22	16.95	1.37	1.29
5.123 84	17.13	1.5	1.37
6.381 61	17.38	1.69	1.49
7.105 69	17.54	1.82	1.58
7.899 69	17.71	1.97	1.69
8.769 58	17.89	2.15	1.83
9.722 85	18.08	2.43	2.02
10.0233	18.15	2.49	2.08
11.1143	18.38	2.73	2.28
12.3647	18.51	3.03	2.55
13.7796	18.59	3.3	2.86
15.4485	18.58	3.67	3.25
17.3714	18.57	3.92	3.69
19.6146	18.52	4.43	4.29
22.2785	18.37	5.01	5.04
24.3931	18.19	5.45	5.64
28.1087	17.81	6.2	6.7
32.5758	17.31	7.16	7.94
37.9207	16.73	8.3	9.4
44.4909	16.08	9.7	11.2
52.1708	15.42	11.4	13.3
61.5047	14.74	13.6	16.0
72.3591	14.2	16.4	19.1
85.1185	13.49	19.4	22.6
100.002	12.92	23.6	27.2
117.286	12.41	29.1	33.0
137.215	11.92	34.6	40.4
160.059	11.51	43.1	49.4
186.055	11.15	54.0	60.6
215.423	10.84	68.0	75.0

III. EXPERIMENTAL METHODS

Measurement of the mobility of helium ions in neon poses few problems. Although the ionization potential of helium is higher than that of neon, charge transfer occurs only by the very slow radiative charge transfer channel. The rate coefficient for the radiative charge transfer has been measured¹¹ and has been calculated,¹² and the emission of photons during the collisions has been observed.¹³ Since charge transfer occurs only in approximately one of 10⁶ collisions its effect on ion transport is completely negligible.

The mobilities were measured using two different types of ion drift tube apparatus. For room-temperature measurements we used a selected ion drift apparatus, consisting of a differentially pumped electron-impact ion source, an injection mass filter to select ⁴He⁺ ions, a drift section of length 35.66 cm, and finally a mass analyzer and ion detection section. This apparatus has been described in more detail earlier.¹⁴ Measurements at liquid-nitrogen temperature were carried out in the variable-temperature drift tube that also has been described previously.¹⁵ The variable-temperature drift tube has a somewhat shorter drift length and lacks the injection mass filter, neither of which is essential for the present work. Experimental procedures were the same with both apparatus. Mobilities are inferred in the standard manner from the measured transit times of pulses of ions through the drift tube.

In general, drift-tube mass spectrometers of fixed drift length such as used here have somewhat lower overall preci-

sion for measurements of mobilities than drift tubes of variable length. Errors arise from so-called "end effects"¹¹ which are difficult to take into account accurately. Based on past experience, we estimate systematic errors arising from end effects to be less than about 3% at low values of E/n_0 , and only slightly larger at high E/n_0 . Measurements of gas pressures were made using a precise capacitance manometer and should be accurate to better than 1%. All gases used were of ultrahigh purity. Mass analysis indicated that the gas purity was better than 1 ppm.

IV. EXPERIMENTAL RESULTS

Measured values of the reduced mobility of helium ions in neon are shown in Figs. 1 and 2 as a function of the field-to-gas-density ratio E/n_0 . Figure 1 shows the room-temperature data (the actual temperatures varied from 295 to 297 K) while data taken at 77 K are plotted in Fig. 2. Different data symbols are used to distinguish data at different gas densities; as expected, the reduced mobilities are independent of gas density.

The solid lines drawn through the data points represent the results of the calculations described in Sec. II. No adjustments or normalizations have been applied to either the ex-

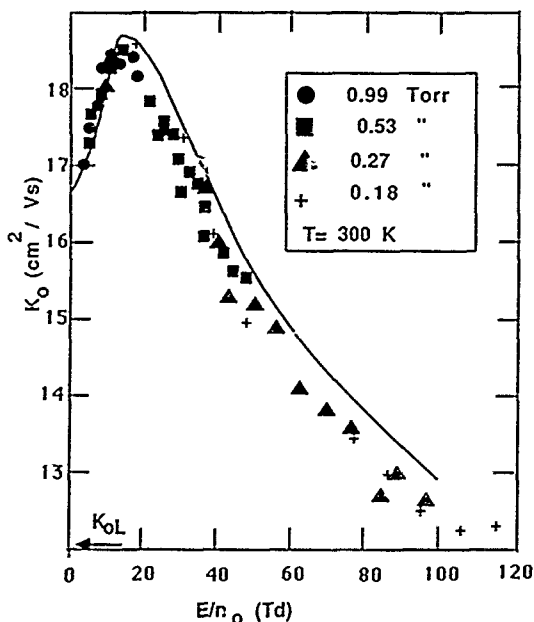


FIG. 1. Measured reduced mobilities of K_0 of He^+ ions in neon at a gas temperature of 300 K, as a function of E/n_0 . Different data symbols refer to the experimental pressures listed in the insert. The solid line represents the computed values.

perimental data or the theoretical results. The arrows shown at $E/n_0 = 0$ indicate the "Langevin" value of the reduced mobility ($K_{0L} = 12.04 \text{ cm}^2/\text{Vs}$), i.e., the temperature and E/n_0 independent mobility which would result from pure polarization scattering. As one might expect, the Langevin model is not applicable in this case, although in the limit of low E/n_0 and at 77 K the measured values approach the Langevin value.

The agreement between the theoretical calculations and the measured data is remarkably good at 77 K, but a small systematic discrepancy seems to be present at high E/n_0 in the room-temperature data. It appears likely that the 300 K data are subject to a small error due to "end effects."

V. CONCLUSIONS

The goal of this study was to test the accuracy of the $\text{He}^+ - \text{Ne}$ potentials derived from spectroscopic measurements by using those potentials to compute ion mobilities and comparing calculated results to measured data. It has been shown that the mobilities calculated using those potentials as input parameters are in very good agreement with experiment. Alternatively, the agreement may also be seen as corroboration for the assumptions made in the transport theories which were used to compute the mobilities. Finally, as helium and neon are employed frequently in many electrical discharge devices, the measured mobilities may find some useful applications.

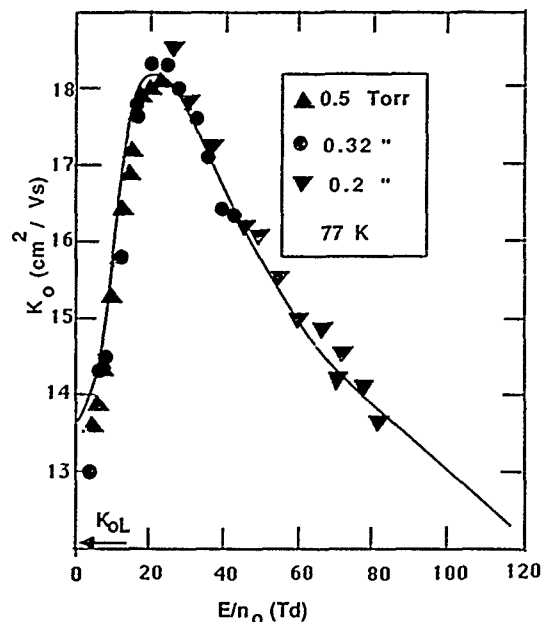


FIG. 2. Measured reduced mobilities K_0 of He^+ ions in neon at a gas temperature of 77 K, as a function of E/n_0 . Different data symbols refer to the experimental pressures listed in the insert. The solid line represents the computed values.

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