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The Mobility of Helium Molecular Ions in Helium*

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A theoretical study of the low field mobility of He_2^+ in its parent gas is described. Forces between He_2^+ and He are calculated by means of perturbation theory. Determination of the scattering phase shifts then yields the momentum transfer cross section as a function of collision energy. Use of the Chapman-Enskog theory of diffusion permits the calculation of the mobility as a function of temperature.

The temperature variation of the mobility of He_2^+ observed by Tyndall and Pearce is analyzed by means of classical theories, yielding an effective potential for the He_2^+-He interaction. The discrepancy between theoretical and experimental mobility is ascribed to certain defects in the calculated potential. When account is taken of ionic clustering, the observed temperature dependence is explained on the basis of a simple potential model.

I. INTRODUCTION

ACCURATE measurements by Tyndall and Powell[1] yielded a value of 21.4 cm^2/volt sec for the mobility of helium ions in helium gas at normal pressure and room temperature. Massey and Mohr[2] made a quantum-theoretical calculation of the mobility of He^+ in helium and deduced a value of 12 cm^2/volt sec. The apparent contradiction between theory and experiment remained unexplained for many years and was tentatively resolved by the suggestion of Meyerott[3] that the ions observed by Tyndall and Powell were molecular rather than atomic. Owing to the smaller probability for charge transfer between He_2^+ and He than between He^+ and He, the molecular ion is expected to be the the more mobile ion.

Mass-spectrographic studies by Arnot and M'Ewen[4] and Hornbeck and Molnar[5] have shown that He_2^+ might be expected to be more abundant than He^+ under the conditions prevailing in the mobility experiment. Phelps and Brown[6] measured the mobilities of He^+ and He_2^+, while at the same time identifying the ions with a mass spectrograph. This is the only experiment in which an identification of ions is made simultaneously with the mobility determination. Their results confirm the interpretation suggested by Meyerott. Other time-of-flight measurements of the mobility of these ions have been made by Hornbeck[7] and Chanin and Biondi[8] with results in good agreement with previous experiment and theory. The present work was undertaken in an effort to demonstrate that the larger observed mobility is consistent with theoretical expectations for He_2^+.

The mobility is related to the coefficient of diffusion by the expression

$$K=qD_{12}/\kappa T. \tag{1}$$

The Chapman-Enskog[9] formula for the coefficient of diffusion of ion 1 through gas composed of atom 2 is

$$D_{12}=\frac{3\pi^{1/2}}{16n}\left(\frac{2\kappa T}{m}\right)^{7/2}\frac{1+\epsilon_0}{\mathcal{P}_{12}}, \tag{2}$$

where q is the ionic charge, n is the total molecular density, m is the reduced mass of ion and atom, and ϵ_0 is a small quantity which depends on the form of the ion-atom potential and their relative masses. ϵ_0 is zero for a potential which varies inversely as the fourth power of the separation and has a maximum value of the order of 0.1 for a hard sphere potential. $\mathcal{P}_{12}$ depends on the dynamics of a collision between the ion and atom;

$$\mathcal{P}_{12}=\int_0^\infty Q_M(v)v^5\exp(-mv^2/2\kappa T)dv, \tag{3}$$

where v is the relative velocity at large separation and Q_M is the momentum transfer cross section (also called the diffusion cross section):

$$Q_M=2\pi\int_0^\infty(1-\cos\theta)bdb. \tag{4}$$

Here θ stands for the angle of deflection occurring as a result of a collision, and b is the impact parameter. If the collision is treated on the basis of quantum theory, the momentum transfer cross section becomes

$$Q_M=\frac{4\pi}{k^2}\sum_0^\infty(l+1)\sin^2(\eta_l-\eta_{l+1}), \tag{5}$$

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[8] L. M. Chanin and M. A. Biondi, paper presented at the Conference on Gaseous Electronics, Princeton, New Jersey (September, 1952).

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where $k=mv/\hbar$ and the η_l's are the scattering phase shifts.

II. POTENTIAL BETWEEN MOLECULAR ION AND ATOM

Because of the relatively low velocities with which thermal collisions take place, we may employ stationary state perturbation theory to calculate the interaction between a molecular ion and a normal atom, that is,

$$\Delta E(R)=(\Delta E)_1+\sum_n{}' \frac{|\mathcal{V}_{0n}|^2}{E_0-E_n}+\cdots. \tag{6}$$

The first-order exchange energy $(\Delta E)_1$ is predominant for small separations, while at large separations the second-order forces are of primary importance. This permits the use of an approximate form, valid at large separations, for the classical interaction in the calculation of the second-order forces.

First-Order Force

Consider the interaction of two atomic systems, 1 and 2, containing ν_1 and ν_2 electrons. The total Hamiltonian is

$$H=H_1+H_2+H', \tag{7}$$

where H' is the interaction potential. We may construct antisymmetrized state functions from products of one electron orbitals,

$$\varphi_1=u_1^{(1)}(1)\alpha(1)u_2^{(1)}(2)\beta(2)\cdots u_{\nu_1}^{(1)}(\nu_1)\beta(\nu_1),$$

as follows:

$$\Psi^{(1)}=\sum_{\lambda_1}(-1)^{\lambda_1}P_{\lambda 1}\varphi_1;\quad \Psi^{(2)}=\sum_{\lambda_2}(-1)^{\lambda_2}P_{\lambda 2}\varphi_2,$$

where $P_{\lambda 1}$ is the operator which permutes coordinates of two electrons within φ_1 (intra-atomic).

Our total function must be antisymmetric with respect to interchange of the coordinates of *any* two electrons in the composite system. It is obtained by applying the interatomic antisymmetrizing operator, as follows:

$$\begin{aligned}\Psi&=\sum_x(-1)^xP_x\Psi^{(1)}\Psi^{(2)}\\ &=\sum_{x,\lambda_1,\lambda_2}(-1)^{x+\lambda_1+\lambda_2}P_xP_{\lambda 1}P_{\lambda 2}\varphi_1\varphi_2=\sum_\lambda(-1)^\lambda P_\lambda\varphi_1\varphi_2,\end{aligned}$$

where P_x is the operator which permutes coordinates of pairs of electrons between 1 and 2 (interatomic) and P_λ is the general type permutation operator (inter- or intra-atomic).[10] From the definition of $\bar{H}$ as

$$\bar{H}=\int\Psi^*H\Psi\bigg/\int\Psi^*\Psi, \tag{8}$$

and the symmetry of the total Hamiltonian with respect to interchange of the coordinates of any two electrons, we obtain the following reduction in terms of orbitals:

$$\bar{H}=\frac{\displaystyle\int\sum_{\lambda_1,\lambda_2}(-1)^{\lambda_1+\lambda_2}(P_{\lambda 1}P_{\lambda 2}\varphi_1{}^*\varphi_2{}^*)\sum_x(-1)^xP_xH\varphi_1\varphi_2}{\displaystyle\int\sum_{\lambda_1,\lambda_2}(-1)^{\lambda_1+\lambda_2}(P_{\lambda 1}P_{\lambda 2}\varphi_1{}^*\varphi_2{}^*)\sum_x(-1)^xP_x\varphi_1\varphi_2}. \tag{9}$$

These integrations are taken over the spin and space coordinates of the $\nu_1+\nu_2$ electrons.

In general, the orbitals used are not exact solutions to the Schrödinger equations for the individual systems. They are variational functions which minimize the internal energies and satisfy the equations:

$$H_1\Psi^{(1)}=\bar{H}_1\Psi^{(1)}+\omega_1;\quad H_2\Psi^{(2)}=\bar{H}_2\Psi^{(2)}+\omega_2. \tag{10}$$

Here $\bar{H}_1$, $\bar{H}_2$ are the minimized internal energies, and ω_1, ω_2 are the unknown correction functions which are orthogonal to $\Psi^{(1)}$, $\Psi^{(2)}$, respectively. This orthogonality is required because of the definition of $\bar{H}_1$ and $\bar{H}_2$ as

$$\bar{H}=\int\Psi^{(1)*}H_1\Psi^{(1)}\bigg/\int\Psi^{(1)*}\Psi^{(1)},$$

$$\bar{H}_2=\int\Psi^{(2)*}H_2\Psi^{(2)}\bigg/\int\Psi^{(2)*}\Psi^{(2)}.$$

Inserting (10) into (9), we have

$$\bar{H}=\bar{H}_1+\bar{H}_2+\bar{H}'+\bar{L},$$

where

$$\bar{H}'=\frac{\displaystyle\int\sum_{\lambda_1,\lambda_2}(-1)^{\lambda_1+\lambda_2}(P_{\lambda 1}P_{\lambda 2}\varphi_1{}^*\varphi_2{}^*)\sum_x(-1)^xP_xH'\varphi_1\varphi_2}{\displaystyle\sum_{\lambda_1,\lambda_2}(-1)^{\lambda_1+\lambda_2}(P_{\lambda 1}P_{\lambda 2}\varphi_1{}^*\varphi_2{}^*)\sum_x(-1)^xP_x\varphi_1\varphi_2}$$

and (11)

$$\bar{L}=\frac{\displaystyle\int\sum_{\lambda_1,\lambda_2}(-1)^{\lambda_1+\lambda_2}(P_{\lambda 1}P_{\lambda 2}\varphi_1{}^*\varphi_2{}^*)\sum_x(-1)^xP_x(\omega_1\varphi_2+\omega_2\varphi_1)}{\displaystyle\int\sum_{\lambda_1,\lambda_2}(-1)^{\lambda_1+\lambda_2}(P_{\lambda 1}P_{\lambda 2}\varphi_1{}^*\varphi_2{}^*)\sum_x(-1)^xP_x\varphi_1\varphi_2}.$$

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[10] The present analysis follows a procedure for computing exchange forces suggested by H. Margenau at the 1951 Office of Naval Research Conference on Shelter Island.

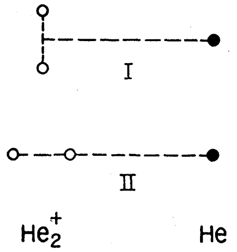

FIG. 1. The two extreme relative orientations between He_2^+ and He.

The first-order perturbation energy is given by

$$(\Delta E)_1=\bar{H}(R)-\bar{H}_1(\infty)-\bar{H}_2(\infty)=\bar{H}'+\bar{L}.$$

Since the ω's are not known, and they may be assumed to be small, $\bar{L}$ is neglected and $(\Delta E)_1$ is approximated by $\bar{H}'$.

In view of Pauling's[11] variational treatment of the helium molecular ion, the ground state of He_2^+ is taken to be represented by the following unsymmetrized product of one-electron orbitals:

$$\varphi_1=a(1)\alpha(1)\{a(2)-b(2)\}\beta(2)b(3)\alpha(3), \tag{12}$$

where

$$a(1)=Z^{\frac{3}{2}}\pi^{-\frac{1}{2}}e^{-Zr_{a1}}, \quad b(1)=Z^{\frac{3}{2}}\pi^{-\frac{1}{2}}e^{-Zr_{b1}},$$

$Z=1.833$, and the electron-nuclear distances r_{a1}, r_{b1} are in units of Bohr radii. A simple variational function for the helium atom contains the effective nuclear charge of $Z'=1.6875$, the unsymmetrized product of orbitals being

$$\varphi_2=c(4)\alpha(4)c(5)\beta(5). \tag{13}$$

Expressions (12) and (13) are used in connection with (11) to obtain $\bar{H}'$. Integration over spin coordinates reduces the number of terms in the numerator and denominator of (11) from 120 to 12. This reduction still leaves a complicated expression for $\bar{H}'$ because of the many terms entering H':

$$H'=-Z_ae^2\left(\frac{1}{r_{a4}}+\frac{1}{r_{a5}}\right)-Z_be^2\left(\frac{1}{r_{b4}}+\frac{1}{r_{b5}}\right)$$
$$-Z_ce^2\left(\frac{1}{r_{c1}}+\frac{1}{r_{c2}}+\frac{1}{r_{c3}}\right)+Z_ce^2\left(\frac{Z_a}{R_{ac}}+\frac{Z_b}{R_{bc}}\right)$$
$$+e^2\left(\frac{1}{r_{14}}+\frac{1}{r_{15}}+\frac{1}{r_{24}}+\frac{1}{r_{25}}+\frac{1}{r_{34}}+\frac{1}{r_{35}}\right), \tag{14}$$

where $Z_a=Z_b=Z_c=2$ and the various distances are labelled in the conventional notation.

The quantity $\bar{H}'$ was calculated for two relative orientations of the molecular ion and atom (Fig. 1)—(I) the atom lying on the perpendicular bisector of the molecular axis, and (II) the atom lying along the extension of the molecular axis. All but one of the two-center integrals which appear may be treated exactly. The three-center integrals require approximations for their evaluation. The approximations used are those applied by Margenau[12] in the calculation of forces between two hydrogen molecules and between a hydrogen molecule and a hydrogen atom.

The results of the numerical evaluation of $\bar{H}'$ for the two orientations may be very closely represented by the following exponential functions:

$$\bar{H}'_{\mathrm{I}}=32.0e^{-2.67(R/a_0)}, \quad \bar{H}'_{\mathrm{II}}=774e^{-2.90(R/a_0)},$$

the unit of energy being e^2/a_0.

Second-Order Forces

The classical interaction for large separations may be expressed in a form simpler than (14). A Taylor expansion[13] of the interaction between the two charge clouds corresponding to ion and atom yields

$$\mathcal{V}=\sum_{ij} e_i\epsilon_j\left[\frac{1}{R}-\frac{1}{R^2}(\zeta_j-z_i)+\frac{1}{R^3}\{-\tfrac{1}{2}(\xi_j-x_i)^2\right.$$
$$\left.-\tfrac{1}{2}(\eta_j-y_i)^2+(\zeta_j-z_i)^2\}+\cdots\right], \tag{15}$$

where e_i; x_i, y_i, z_i and ϵ_j; ξ_j, η_j, ζ_j are the elements of charge and their coordinates relative to the centers of the atom and molecular ion, respectively, and R is the distance between centers. The Z axis is taken to be along the line of centers.

An exact evaluation of $\sum_n'[|\mathcal{V}_{0n}|^2/(E_0-E_n)]$ is impossible because little is known about the excited states of the molecular ion. A simplified treatment is to restrict the quantum calculation to the helium atom and regard the molecular ion as an external perturbation. This is a simplifying picture inasmuch as the excited states of the system will now be those of the atom alone, rather than of the atom plus ion. The summation over the charge distribution of the molecular ion isc onverted to an integral, yielding for the second-order perturbation energy:

$$(\Delta E)_2=\sum_n{}' \int \Psi^*(He_2^+)|\mathcal{V}_{0n}|^2\Psi(He_2^+)/(E_0-E_n),$$

where E_n now refers to helium atomic states and $\Psi(He_2^+)$ is the ground-state wave function for the helium molecular ion.

In the helium atom all the one-electron excited states lie between 20.5 and 24.5 volts above the ground state. It seems reasonable to replace the energy denominator by an average value lying somewhere in the neighborhood of the ionization energy. The functions which are the base of the matrix elements $\mathcal{V}_{0n}$ form a complete set, requiring the following matrix relation to hold:

$$\sum_n{}'|\mathcal{V}_{0n}|^2=(\mathcal{V}^2)_{00}-(\mathcal{V}_{00})^2.$$

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[11] L. Pauling, J. Chem. Phys. **1**, 56 (1933).

[12] H. Margenau, Phys. Rev. **64**, 131 (1943); **66**, 303 (1944).

[13] H. Margenau, Revs. Modern Phys. **11**, 1 (1939).

The term $\mathcal{V}_{00}$ vanishes, leaving

$$(\Delta E)_2 = -\frac{1}{\bar{E}} \int \Psi^*(\mathrm{He}_2{}^+)(\mathcal{V}^2)_{00}\Psi(\mathrm{He}_2{}^+). \tag{16}$$

Squaring $\mathcal{V}$ and retaining only those terms that do not vanish on integration, we have

$$\mathcal{V}^2 = \frac{e^2}{R^4}[\textstyle\sum_i e_i z_i]^2 + \frac{e^2}{4R^6}[\textstyle\sum_i e_i(x_i{}^2+y_i{}^2-2z_i{}^2)]^2 + \frac{1}{R^6}[\textstyle\sum_{ij} e_i \epsilon_j(\boldsymbol{\varrho}_j\cdot\mathbf{r}_i - 3\zeta_j z_i)]^2 + \cdots. \tag{17}$$

When dealing with second-order forces between two neutral molecules, only the third term in the preceding expression exists. It is the well-known Van der Waals interaction. The first term in (17) leads to the polarization potential, which classically arises from the interaction of the point charge of the ion with the induced dipole of the neutral atom. Margenau[14] first called attention to the importance of the second term in the interaction between an ion and a neutral atom or molecule. It represents the interaction of the point charge of the ion with the induced quadruple of the neutral atom.

Using the ground-state function,

$$\Psi(\mathrm{He}) = (1/\sqrt{2})\,|c(1)\alpha(1)\;c(2)\beta(2)|,$$

we obtain for the second-order interaction energy:

$$-\frac{e^4}{\bar{E}}\left[\frac{2}{3}\frac{(r^2)_{00}}{R^4} + \frac{2}{5}\frac{(r^4)_{00}}{R^6} + \frac{2}{3}\frac{(r^2)_{00}\Theta}{R^6}\right],$$

where

$$(r^2)_{00} = \int r_{c1}{}^2 c^2(1)d\tau_1, \quad (r^4)_{00} = \int r_{c1}{}^4 c^2(1)d\tau_1$$

and

$$\Theta = \int \Psi^*(\mathrm{He}_2{}^+)[(\textstyle\sum_j\xi_j)^2 + (\sum_j\eta_j)^2 + 4(\sum_j\zeta_j)^2]\Psi(\mathrm{He}_2{}^+).$$

The index j labels the three electrons in the molecular ion. The contribution of the charge of the nuclei to Θ vanishes because the sum of the nuclear coordinates relative to the center of the molecular ion vanishes. The quantity Θ depends on the relative orientation (I or II in Fig. 1) as follows:

$$\Theta_{\mathrm{I}} = \mathcal{A} + 5\mathcal{B} = 5.90a_0{}^2, \quad \Theta_{\mathrm{II}} = 4\mathcal{A} + 2\mathcal{B} = 8.51a_0{}^2,$$

where, by symmetry,

$$\mathcal{A} = \int \Psi_{\mathrm{I}}{}^*(\mathrm{He}_2{}^+)(\textstyle\sum_j \xi_j)^2\Psi_{\mathrm{I}}(\mathrm{He}_2{}^+) = \int \Psi_{\mathrm{II}}{}^*(\mathrm{He}_2{}^+)(\sum_j \zeta_j)^2\Psi_{\mathrm{II}}(\mathrm{He}_2{}^+),$$

$$\mathcal{B} = \int \Psi_{\mathrm{I}}{}^*(\mathrm{He}_2{}^+)(\textstyle\sum_j \zeta_j)^2\Psi_{\mathrm{I}}(\mathrm{He}_2{}^+) = \int \Psi_{\mathrm{II}}{}^*(\mathrm{He}_2{}^+)(\sum_j \xi_j)^2\Psi_{\mathrm{II}}(\mathrm{He}_2{}^+),$$

and

$$\Psi(\mathrm{He}_2{}^+) = [12(1-\Delta)(1-\Delta^2)]^{-\frac{1}{2}} \times |a(1)\alpha(1)\;\{a(2)-b(2)\}\beta(2)\;b(3)\alpha(3)|,$$

$$\Delta = \int a(1)b(1)d\tau_1.$$

Furthermore, from the quantum theory of the Stark effect the static polarizability of helium is

$$s = (4/3)e^2(r^2)_{00}/\bar{E},$$

from which it follows that

$$(\Delta E)_2 = -\frac{se^2}{2R^4}\left(1 + 1.59\frac{a_0{}^2}{R^2} + \frac{\Theta}{R^2}\right). \tag{18}$$

It is worth noting that the Van der Waals term is considerably larger than the monopole-induced quadrupole term. The experimentally determined polarizability[13] of helium gas, 0.205×10^{-24} cm^3, is used in (18) to determine the numerical value of $(\Delta E)_2$.

We are interested in determining the probability that the molecular ion will undergo an internal change of state in the course of a thermal collision with a gas atom. The general condition[15] for the collision to be adiabatic with respect to a given transition, be it an electronic, vibrational, or rotational transition, is

$$\Delta\mathcal{E}/h\tau_c \gg 1,$$

where $\Delta\mathcal{E}$ is the energy of transition and τ_c is the average collision time. From band spectra,[16] $\Delta\mathcal{E}$ has been found to be approximately 0.20 and 0.0009 ev for vibrational and rotational transitions in $\mathrm{He}_2{}^+$. For average thermal velocities, the adiabatic condition is satisfied for vibrational transitions, while nonadiabaticity prevails for rotational transitions. Hence, if the molecular ion is formed in its ground vibrational state, it will remain there during its transit through the gas.

The Chapman-Enskog theory of diffusion as outlined in the Introduction is true only for rigid, spherically symmetrical molecules. Hence, it is obviously not immediately applicable to the present problem. Pidduck[17] has investigated the effect on the coefficient of diffusion when rigid molecules are replaced by molecules possessing a rotational degree of freedom. He finds that there is a correction to the coefficient of diffusion, if both types of molecules, 1 and 2, are capable of rotation. In the case that one type of molecule can rotate and the

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[14] H. Margenau, Phil. Sci. **8**, 603 (1941).

[15] H. S. W. Massey, Repts. Progr. Phys. **12**, 248 (1949).

[16] W. Weizel and E. Pestel, Z. Physik **56**, 197 (1929).

[17] F. B. Pidduck, Proc. Roy. Soc. (London) **A101**, 101 (1922); reference 9, p. 214.

other cannot, there is *no* correction to the formula for rigid molecules. In the present case of the diffusion of He_2^+ through He, the helium atoms possess no rotational degrees of freedom and, consequently, the original formula is valid.

There still remains the requirement of spherical symmetry for the applicability of the diffusion formula. To meet this we choose an average potential which lies between the potentials corresponding to the extreme relative orientations, I and II. The orientation of the molecular ion relative to the atom affects the interaction potential in both the first- and second-order terms. The entire first-order term $\bar{H}'$ and the part involving Θ in the second-order expression are orientation dependent. The mean time between collisions is much larger than the collision time, while the time for one rotation is about equal to the collision time. Hence, there is very little correlation between the molecular orientations in two successive collisions with gas atoms. Two limiting cases may be considered; namely, the rotational period very small or very large compared to the collision time. When the rotation is very rapid, the incident atom will see only the longest range potential, that is, the one corresponding to II (Fig. 2). For slow rotation, the effective potential lies somewhere between I and II (Fig. 2). If the molecular rotation is considered classically, the approximate ratio of rotation time to collision time is 5. In the following sections, we confine our attention to the limiting case of slow rotation.

Let us introduce a system of spherical coordinates with the origin at the center of the molecular ion and the polar axis along the line joining the centers of molecular ion and atom. The polar angle χ lies between the molecular and polar axes. Our case I (Fig. 1) corresponds to $\chi=\pi/2$ or $3\pi/2$, while II corresponds to $\chi=0$ or π. If $\mathcal{V}$ is a general interaction potential which has the two extreme values, $\mathcal{V}_{\rm I}(R)$ and $\mathcal{V}_{\rm II}(R)$, we may interpolate for intermediate orientations by assuming that it has elliptical dependence, that is,

$$\mathcal{V}^2(\chi, R)\left[\frac{\sin^2\chi}{\mathcal{V}_{\rm I}^2(R)}+\frac{\cos^2\chi}{\mathcal{V}_{\rm II}^2(R)}\right]=1.$$

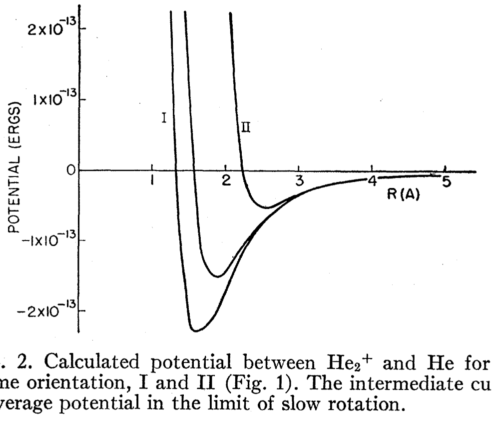

FIG. 2. Calculated potential between He_2^+ and He for each extreme orientation, I and II (Fig. 1). The intermediate curve is the average potential in the limit of slow rotation.

It should be pointed out that this choice of interpolation formula is quite arbitrary and is based largely upon the reasonable assumption that $\mathcal{V}_{\rm I}(R)$ and $\mathcal{V}_{\rm II}(R)$ are extremals of $\mathcal{V}(\chi, R)$. The effective spherically symmetrical potential is now obtained by averaging over all orientations,

$$\langle\mathcal{V}(R)\rangle_{\rm Av}=\int_0^{\pi/2}\mathcal{V}(\chi, R)\sin\chi d\chi$$

$$=\frac{\mathcal{V}_{\rm I}}{(1-\mathcal{V}_{\rm I}^2/\mathcal{V}_{\rm II}^2)^{\frac{1}{2}}}\sin^{-1}\left(1-\frac{\mathcal{V}_{\rm I}^2}{\mathcal{V}_{\rm II}^2}\right)^{\frac{1}{2}}.$$

The azimuthal angle does not enter because of symmetry.

Using this method of averaging, we obtain

$$\langle\bar{H}'\rangle_{\rm Av}=49.0e^{-2.67(R/a_0)},\text{ in } e^2/a_0;\quad \langle\Theta\rangle_{\rm Av}=6.59a_0^2.$$

On combining the first- and second-order contributions, we obtain as a total averaged interaction energy:

$$V(R)=21.3\times10^{-10}e^{-5.06R}-\frac{2.36\times10^{-12}}{R^4}-\frac{5.41\times10^{-12}}{R^6},$$

in ergs, where R is in Angstrom units. This is plotted in Fig. 2.

III. METHODS APPLIED TO MOBILITY DETERMINATION

The collision between ion and atom will be essentially classical in the temperature range 20–500°K, since the de Broglie wavelength is very small compared to the effective scattering radius. Hence, the momentum transfer cross section may be obtained with the use of (4) or (5). We choose to carry out the cross-section calculation by means of the quantum formulation, so as to make clear the modifications needed in the very low temperature region where classical collisions do not take place.

The phase shifts required in (5) may be obtained from the WKB solution of the radial wave equation

$$d^2G_l/dR^2+[k^2-U(R)-l(l+1)/R^2]G_l=0, \qquad (19)$$

where $k=mv/\hbar$ and $U(R)=(2m/\hbar^2)V(R)$. In this approximation the phase shift is

$$\eta_l=\int_{R_l}^{\infty}[g_l^{\frac{1}{2}}-k]dR-kR_l+\tfrac{1}{2}\pi[l(l+1)]^{\frac{1}{2}}, \qquad (20)$$

where $g_l=k^2-U(R)-l(l+1)/R^2$ and R_l is the largest positive zero of g_l. Because of the complicated form of g_l, it is necessary to perform the integration

$$\int_{R_l}^{\infty}[g_l^{\frac{1}{2}}-k]dR$$

numerically. Different approximation methods are applicable in calculating the phase shifts, depending on whether l is large or small.

(a) Small Values of l

Equation (20) may be rewritten in the form:

$$\eta_l=\int_{R_l}^{\infty}\left\{\omega^{\frac{1}{2}}\left(1-\frac{l(l+1)}{\omega R^2}\right)^{\frac{1}{2}}-k\right\}dR$$

$$-kR_l+\frac{1}{2}\pi[l(l+1)]^{\frac{1}{2}},\quad(21)$$

where $\omega=k^2-U(R)$. For low values of l, $l(l+1)/\omega R^2$ is much smaller than unity over the whole range of R from R_l to ∞. At R_l, $l(l+1)/\omega R^2$ is equal to 1, but it rapidly decreases in value as R exceeds R_l. Expanding $(1-l(l+1)/\omega R^2)^{\frac{1}{2}}$ yields

$$\eta_l=\int_{R_l}^{\infty}(\omega^{\frac{1}{2}}-k)dR$$

$$+\int_{Rl}^{\infty}\omega^{\frac{1}{2}}\left[-\frac{1}{2}\frac{l(l+1)}{\omega R^2}-\frac{1}{8}\frac{l^2(l+1)^2}{\omega^2R^4}\cdots\right]dR$$

$$-kR_l+\tfrac{1}{2}\pi[l(l+1)]^{\frac{1}{2}}.\quad(22)$$

The quick convergence of this expansion fails when $l(l+1)/\omega R^2$ is comparable to unity over a large range of R. Equation (22) is much more useful for the numerical work than (20) because the factor containing l may be removed from the integral, requiring only about three or four numerical integrations for a given energy. In (20), $g_l^{\frac{1}{2}}$ has to be numerically integrated for each value of l.

It is convenient to divide the range of integration in (22) at some value R'' large enough (taken to be $6A$) so that $V(r)$ for $R>R''$ is essentially the polarization potential only. The integrals over the range from R'' to ∞ are evaluated by analytic means.

(b) Large Values of l

The basic form for the phase shift in the WKB approximation is

$$\eta_l=\int_{Rl}^{\infty}\left[k^2-U(R)-\frac{l(l+1)}{R^2}\right]^{\frac{1}{2}}dR$$

$$-\int_{R'l}^{\infty}\left[k^2-\frac{l(l+1)}{R^2}\right]^{\frac{1}{2}}dR,$$

where the lower limits are the largest positive zeros of the respective intergands. When l is very large, $U(R_l)$ is small compared with $l(l+1)/R_l^2$, so that we may consider the lower limits in the integrals to be equal. Expanding the square roots, we obtain for the phase shift:

$$\eta_l\cong-\tfrac{1}{2}\int_{(l+\frac{1}{2})/k}^{\infty}\frac{U(R)}{[k^2-(l+\frac{1}{2})^2/R^2]^{\frac{1}{2}}}dR,$$

after letting $l(l+1)\cong(l+\frac{1}{2})^2$. Only the polarization potential, $-c/R^4$, is significant at these large values of R_l', giving

$$\eta_l(\mathrm{WKB})=\pi mck^2/[4\hbar^2(l+\tfrac{1}{2})^3].\quad(23)$$

This result was obtained by Massey and Mohr,[2] who showed, by comparison with more exact methods, that (23) is very accurate if the phase shifts are less than 0.5 radian.

The Born approximation is valid when the centrifugal barrier is large compared to the potential at distances of about $[l(l+1)]^{\frac{1}{2}}/k$. This condition is the same as was used in deriving (23) from the WKB approximation. Under these circumstances, the incident particle is blocked by the centrifugal barrier and does not get into the region where the potential is large; the phase shift is then small and may be evaluated by the Born formula

$$\eta_l(\mathrm{Born})=-\frac{\pi m}{\hbar^2}\int_0^{\infty}V(R)[J_{l+\frac{1}{2}}(kR)]^2RdR.$$

Again, taking for $V(R)$ the polarization energy only and making use of the formula,[18]

$$\int_0^{\infty}\frac{[J_\mu(x)]^2}{x^\nu}dx=2^{-\nu}\frac{\Gamma(\nu)}{[\Gamma(\frac{1}{2}\nu+\frac{1}{2})]^2}\cdot\frac{\Gamma(\mu-\frac{1}{2}\nu+\frac{1}{2})}{\Gamma(\mu+\frac{1}{2}\nu+\frac{1}{2})}$$

[provided $\mathrm{Re}(2\mu+1)>\mathrm{Re}\nu>0$], we obtain

$$\eta_l(\mathrm{Born})=\frac{\pi mck^2}{4\hbar^2(l+\frac{3}{2})(l+\frac{1}{2})(l-\frac{1}{2})}.\quad(24)$$

Equations (23) and (24) are seen to be almost equal, differing by the fractional amount $1/l(l+\frac{3}{2})$. Since we are dealing with large values of l, this discrepancy is much less than one percent.

(c) Intermediate Values of l

For all collision energies in the thermal range, there is a value of l at which the classical turning point R_l changes discontinuously. This arises from the fact that the scattering potential is not monatonic. The classical turning point is determined by the short-range repulsive potential for small l and by the centrifugal barrier for large l. Figure 3 illustrates the corresponding discontinuity in phase shift, which occurs at $l=23$ for the energy given by $k=6\times10^8$ cm^{-1}. The angular momentum quantum number at which the discontinuity occurs, l_d, increases with increasing energy.

Although the WKB phase shifts are not too accurate

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[18] W. Magnus and F. Oberhetinger, *Special Functions of Mathematical Physics* (Chelsea Publishing Company, New York, 1949), p. 35.

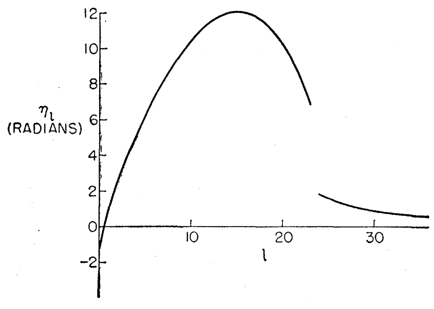

FIG. 3. Calculated phase shifts for $k=6\times 10^8$ cm^{-1}.

for values of l in the vicinity of l_d, the error introduced into the differences of successive phase shifts on either side of l_d is of second order. However, the discontinuity in η_l is, in general, of the order of $\pi/2$ or greater, so that there is a maximum uncertainty of unity in the value of $\sin^2(\eta_{l_d}-\eta_{l_d+1})$. This corresponds to a small range of impact parameters (in the classical scattering problem) where the orbit is almost closed and $\cos\theta$ oscillates very rapidly. Our inability to obtain an accurate value for $\sin^2(\eta_{l_d}-\eta_{l_d+1})$ is a definite limitation of the present method.

For some energies the quantity g_l has three zeros for the first few values of l which are greater than l_d. This case must be treated[19] by joining the WKB solutions across all three zeros. The result obtained from this procedure does not differ appreciably from the case of g_l having one zero; hence we neglect the modification.

The scattering energies at which Q_M is computed correspond to the following values of the parameter k: 2, 4, 6, 8, 10, 12.5×10^8 cm^{-1}. It is convenient to break the summation (5) into three parts,

$$Q_M^{(1)}=\frac{4\pi}{k^2}\sum_{0}^{l_d-1}(l+1)\sin^2(\eta_l-\eta_{l+1}),$$

$$Q_M^{(2)}=\frac{4\pi}{k^2}(l_d+1)\sin^2(\eta_{l_d}-\eta_{l_d+1}),$$

$$Q_M^{(3)}=\frac{4\pi}{k^2}\sum_{l_d+1}^{\infty}(l+1)\sin^2(\eta_l-\eta_{l+1}).$$

The first part, which makes by far the greatest contribution, is evaluated by direct numerical summation. The third part, which is the smallest, may be reduced to a convenient form. For $l>l_d$, $\sin(\eta_l-\eta_{l+1})\cong\eta_l-\eta_{l+1}\cong d\eta_l/d_l$, and using (23) we have

$$Q_M^{(3)}=\frac{4\pi}{k^2}\sum_{l_d+1}^{\infty}(l+1)\left(\frac{d\eta_l}{dl}\right)^2=\frac{M_k}{(l_d+\frac{3}{2})^6}\left[\frac{1}{6}+\frac{1}{14(l_d+\frac{3}{2})}\right],$$

where $M_k=4\pi c(3\pi mk/4\hbar^2)^2$.

The direct evaluation of $Q_M^{(2)}$ is not feasible owing to previously mentioned uncertainties. The correct value of Q_M lies between $Q_M^{(1)}+Q_M^{(3)}$ and $Q_M^{(1)}+Q_M^{(3)}+(4\pi/k^2)(l_d+1)$ since $0\leq\sin^2(\eta_{l_d}-n_{l_d+1})\leq 1$. An interpolation for kQ_M was made between the limiting values, requiring that it assumed the proper classical value for $k=0$. The zero energy value was taken from calculations of Langevin[20] and Hassé,[21] which are discussed in the next section. The validity of this interpolation was confirmed by assigning to $\sin^2(\eta_{l_d}-\eta_{l_d+1})$ its average value of $\frac{1}{2}$ and then noting that kQ_M as a function of k falls very close to its interpolated value.

Q_M can be represented by a functional form most conveniently when it is plotted *versus* $1/k$, the form being

$$Q_M(\text{cm}^2)=148\times 10^{-8}/k-2.90\times 10^{-16}.$$

With the relation $k=mv/\hbar$, Q_M is expressed in terms of v, permitting the evaluation of $\mathcal{P}_{12}$. When use is made of (1) and (2), and the small quantity ϵ_0 is taken to be zero (since predominant force is polarization), the resultant expression for the mobility at constant density (2.52×10^{19}/cm^3) is

$$K_\rho(\text{cm}^2/\text{volt sec})=207/(102-T^{\frac{1}{2}}).$$

This is plotted in Fig. 4 together with the experimental results of Tyndall and Pearce.[22] We estimate an uncertainty of ±5 percent in calculating the mobility from a given potential by the above procedure.

IV. ANALYSIS OF EXPERIMENTAL RESULTS

In Langevin's[20] theory of mobilities the ion-atom potential was taken to be a hard sphere repulsion of radius σ plus a polarization attraction $-c/R^4$ from $R=\sigma$ to ∞. With this model for the potential, the classical scattering angles can be exactly evaluated in terms of complete and incomplete elliptic integrals of the first kind. The resulting formula for the mobility is

$$K=\frac{A(\lambda)}{[\rho(\delta-1)]^{\frac{1}{2}}}\left(1+\frac{m_2}{m_1}\right)^{\frac{1}{2}}, \tag{25}$$

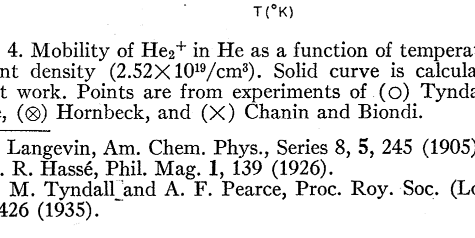

FIG. 4. Mobility of He$_2$$^+$ in He as a function of temperature at constant density (2.52×10^{19}/cm^3). Solid curve is calculated in present work. Points are from experiments of (○) Tyndall and Pearce, (⊗) Hornbeck, and (×) Chanin and Biondi.

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[19] R. A. Buckingham and A. Dalgarno, Proc. Roy. Soc. (London) **A213**, 506 (1952).

[20] P. Langevin, Am. Chem. Phys., Series 8, **5**, 245 (1905).

[21] H. R. Hassé, Phil. Mag. **1**, 139 (1926).

[22] A. M. Tyndall and A. F. Pearce, Proc. Roy. Soc. (London) **A149**, 426 (1935).

where m_1 and m_2 are the masses of ion and atom, ρ is the gas density, δ is the dielectric constant of the gas, and A is a numerical function of the variable

$$\lambda=\left[\frac{8\pi p\sigma^4}{(\delta-1)e^2}\right]^{\frac{1}{2}}=\left(\frac{\kappa T\sigma^4}{c}\right)^{\frac{1}{2}}.$$

The function A is tabulated by Hassé[21] for values of λ from 0 to 4 in intervals of 0.1. It has a maximum value at $\lambda\cong 0.6$. This means that, for a given interaction potential (specified σ and c), the mobility will be a maximum for a given temperature. Reducing σ or increasing c has the effect of increasing the temperature at maximum mobility.

Langevin's expression for the mobility in a gas at constant density is of the form

$$K_\rho=AY,$$

where the constant

$$Y=[e^2/8\pi n\rho c]^{\frac{1}{2}}(1+m_2/m_1)^{\frac{1}{2}}.$$

The parameter λ is defined by $T=\lambda^2S$, with $S=c/\kappa\sigma^4$. Given the values of c and σ, we could calculate the temperature variation of K_ρ and compare it with experiment. Essentially, this is what was done in preceding sections in a more general way. Now it is desired to make use of the experimental values of K_ρ as a function of T to obtain the form of the actual potential.

This can be done very conveniently by means of a method originally employed by Keesom and applied by Pearce[23] and Hoselitz[24] to their experiments on the mobility of alkali ions in the rare gases. Taking the logarithm of the preceding expressions, we have

$$\log K_\rho=\log A+\log Y,\quad \log T=\log(\lambda^2)+\log S.$$

We now plot the experimental values of $\log K_\rho$ *versus* $\log T$. Then $\log A$ as a function of $\log(\lambda^2)$ is plotted to the same scale (Fig. 5). Shifting the theoretical curve over the experimental curve, while keeping their corresponding axes parallel, one may find the position of best fit. The amount that each axis is shifted is equal to $\log Y$ and $\log S$. Knowing Y and S, the best values for the parameters c and σ are calculated. In making the fit to experiment, we assume that the constancy of the observed mobility at 21.4 cm²/volt sec over a temperature range of 200° corresponds to its maximum value. This is reasonable on the basis of the temperature variation of the mobility of other ions in helium and provides for a unique fit between theory and experiment.

Hassé and Cook[25] have derived a formula for mobility using the Chapman-Enskog theory and a potential between ion and gas atom of the form

$$B/R^8-C/R^4.$$

This amounts to a softer repulsion than the hard sphere, the attractive part still consisting of a pure polarization force. It is found that the hard sphere model permits a much closer fit with experiment than is obtained with the Hassé-Cook potential; hence, the latter will not be considered further.

It is of interest to note that Tyndall and Pearce did not attempt to analyze their data in this manner. Believeing their data to be the mobility of helium atomic ions which are subject to charge transfer, they felt, and justifiably so, that the classical Langevin theory would not apply. The current belief that their data corresponds to the mobility of the helium molecular ion removes the possibility of charge transfer and makes the classical theory applicable.

The superposed experimental and theoretical curves are shown in Fig. 5. The experimental curve begins to fall below the Langevin theoretical curve at a temperaature of about 170°K, while there is a good fit in the temperature range from 170° to 480°K. The values for the potential parameters are found to be $\sigma=1.95$A and $c=2.73\times10^{-44}$ erg cm⁴. The corresponding effective potential for He_2^+-He is plotted in Fig. 6 together with the previously calculated potentials. It is to be noted that the "experimental" potential has a longer range repulsion than the calculated one, while the attractive parts of the two curves lie very close together.

A possible explanation for the discrepancy between theory and experiment in Fig. 5 for temperatures below 170°K can be found by taking into account the effect of ionic clustering. The size of the ion cluster is found statistically as a function of temperature by the methods of Bloom and Margenau.[26] For a potential having the values of σ and c determined above, the clustering sets in at about 200°K and increases to give a cluser size of about 70 He atoms at 20°K. The effect of clustering is to reduce the mobility of an ion, owing to the increase in its effective mass.

In the temperature range where clustering occurs, the mobility is influenced primarily by the polarization force, and it is relatively insensitive to changes in the

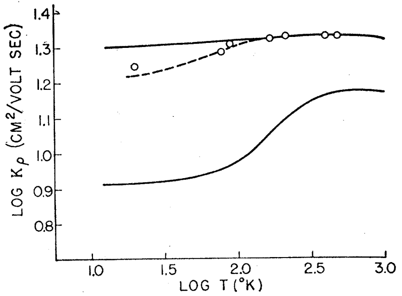

FIG. 5. Log-log plot mobility *versus* temperature corresponding to the best fit of Langevin theory (upper solid curve) to the experimental points (○). The dashed line is the theoretical correction for clustering. The lower solid curve is obtained from the Hassé-Cook theory for arbitrary potential parameters.

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[23] A. F. Pearce, Proc. Roy. Soc. (London) **A155**, 490 (1936).

[24] K. Hoselitz, Proc. Roy. Soc. (London) **A177**, 200 (1940).

[25] H. R. Hassé and W. R. Cook, Phil. Mag. **12**, 554 (1931).

[26] S. Bloom and H. Margenau, Phys. Rev. **85**, 670 (1952).

hard sphere radius. Consequently, the effect of the change in σ caused by clustering will not be very significant compared to the effect of the mass change. The theoretical curve corrected for clustering is also plotted in Fig. 5. The experimental points are seen to lie close to the corrected theoretical curve.

V. CONCLUSIONS

The divergence of the experimental mobilities from the Langevin theory at temperatures below 170°K is interpreted to be largely the result of cluster formation. The close agreement in the range of temperatures from 170° to 480°K, where the ion is unclustered, lends strong support to the essential correctness of the deduced hard sphere-plus-polarization potential.

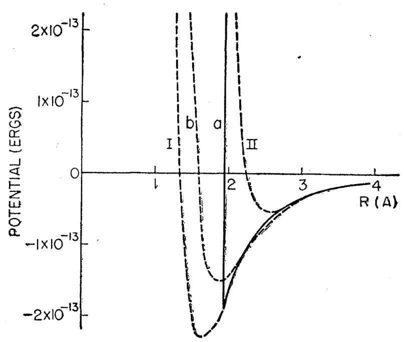

FIG. 6. Potential between He_2^+ and He. (a) Hard sphere-plus-polarization potential obtained from best fit of Langevin theory to experimental data. Curves (b), I, and II are the calculated potentials of Fig. 2.

In comparing the originally calculated mobility with experiment (Fig. 4), the main discrepancy is seen to occur between the slopes of the two curves, rather than between their actual values at particular temperatures. At room temperature, the calculated mobility is 24.2 cm²/volt sec, as compared to the experimental values of 21.4, 20.3, and 22.4 cm²/volt sec given by Tyndall and Pearce, Hornbeck, and Chanin and Biondi. The slope of the experimental curve is essentially zero from 200° to 480°K, while the calculated slope is appreciable. The estimated error in evaluating the mobility once a potential is assigned is smaller than the discrepancy appearing in Fig. 4. We therefore attribute this discrepancy primarily to the difference between our theoretically derived potential and that which has been deduced from experiment (Fig. 6). The latter is assumed to be a good representation of the true average potential between He_2^+ and He. Whereas the observed mobility has its maximum at room temperature, the theoretical mobility is still in the region where the effect of the attractive force predominates, causing the mobility curve to have a positive slope.

The theoretical potential may be at fault for two possible reasons—use of inexact wave functions in the perturbation calculation and an improper method of averaging over orientation. The use of variational wave functions tends to make the repulsive range of the calculated potential somewhat too short. It is well known that the charge distribution of an atom given by the square of its variational wave function is more "pulled in" than the self-consistent charge distribution. The fact that the potential which best fits the data lies between the potentials originally calculated for the two extreme orientations indicates that our quantum-mechanical calculation of the interaction was reasonably good. Apparently our method of averaging over orientations on the basis of slow rotation is not entirely valid, since the molecular ion can make almost a quarter of a rotation during the collision. The "experimental" potential does lie between the theoretical potentials corresponding to the limiting cases of fast and slow rotation (Fig. 6). We may thus conclude with some confidence that the ions observed in the experiments of Tyndall and Powell[1] and Tyndall and Pearce[22] were indeed He_2^+.

It is felt that the neglect of charge transfer between He_2^+ and He is justified. If charge transfer occurred, the resultant He_2 ground state molecule would dissociate, requiring the energy release of about 2.5 ev. This large excess energy makes the process virtually impossible for thermal collisions.

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