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CALCULATION OF LONG RANGE FORCES AND THEIR APPLICATIONS IN DETERMINING GASEOUS PROPERTIES

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ABSTRACT

A discussion of various theoretical and experimental techniques for the calculation of long range interaction between two atomic systems at moderate separation is presented. Some applications of these techniques for obtaining gaseous properties are described. The forces between neutral molecules and metallic surfaces have also been discussed and numerical values of heats of adsorption for a number of systems have been calculated.

INTRODUCTION

Calculations of long range interaction between a pair of atoms or between a pair of molecules are needed in several fields, such as, molecular scattering, transport calculations in gases, atomic spectra and optics. The exact calculation of interaction energy requires a knowledge of the atomic wave functions describing the unperturbed systems in their ground states and the excited states. Except for simple systems like hydrogen and helium atoms, such exact calculations cannot be made at present. Reasonably accurate estimates of the interaction Hamiltonian can, however, be made by making certain simplifying assumptions about the perturbing potential and the interacting systems (see ref. 1). A number of approximate formulae for the leading term in the interaction energy have been developed during the last 30 years. These formulae usually express the interaction energy in terms of such measurable quantities as the refractive index, Lamb shift, stopping power for fast charged particles and Rayleigh scattering cross section. It is the purpose of this report to discuss various techniques for calculating long range interaction between several systems. During these discussions, new techniques for obtaining information of the gaseous properties will be indicated. The subject of physically adsorbed gases on metallic surfaces will also be discussed and heats of adsorption calculated for several commonly used systems.

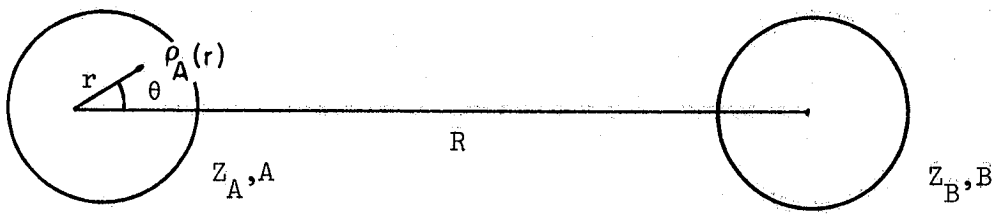
THEORY

Attractive forces can occur between two nonpolar neutral atomic and molecular systems. (In this report,(*) we will be mainly concerned with the atom-atom long range attractive forces.) These forces are very weak and extend out to distances of the order of a few angstroms. A brief discussion of the theory of these interatomic forces is given below. (A more detailed discussion may be found in references 1b and 1c.)

(*)For a brief description of the atom-molecule and molecule-molecule long range forces, see the appendix 1.

(A) Classical Theory of Interaction

Consider two weakly interacting spherical, atomic systems A and B with nuclear charges Z_A and Z_B. Suppose that the systems are neutral and the separation R is sufficiently large ($\gtrsim$ 10 angstroms) to minimize charge overlap but not too large to bring in retardation effects resulting from the finite time for photon exchange. Let $\rho_A(r)$ be the charge element at a distance r from the center of the atomic system A.



The series expansion of the interaction potential, $V_A(R)$, at B due to the system A, in terms of its charge distribution function, $\rho_A(r)$, may be written as follows:

$$V_A(R) = \int \frac{\rho_A(r)\, d\tau}{|R - r|} \tag{1}$$

$$= \sum_{\ell} V_A^{\ell}(R), \text{ if the charge distribution occupies a a limited region of space.}$$

where $$V_A^{\ell}(R) = \frac{1}{R^{\ell + 1}} \int \rho_A(r)\, r^{\ell}\, P_{\ell}(\cos\theta)\, d\tau$$

$$= \frac{1}{R} \int \rho_A(r)\, d\tau, \text{ for spherically symmetrical distribution.}$$

In this equation, ℓ signifies the order of symmetry of the charge distribution function $\rho_A(r)$ and θ is the angle between vectors r and R.

Thus the electrostatic potential to the second order, at B due to A can be written as follows:

$$V_A(R) = \sum_0^2 V_A^{\ell}(R) = \int \frac{\rho_A(r)\, d\tau}{R} + \int \frac{\rho_A(r)\, r \cos\theta\, d\tau}{R^2}$$

$$+ \int \frac{\rho_A(r)\, r^2\, P_2\,(\cos\theta)\, d\tau}{2R^3}$$

$$= \frac{Z_A}{R} + \frac{M_A \cdot R_o}{R^2} + \frac{R_o \cdot D_A \cdot R_o}{2R^3} \qquad (2)$$

Where $M_A = \int \rho_A(r)\, r\, dv$

R_o = unit vector in the direction of R and

$\frac{R_o \cdot D_A \cdot R_o}{2R^3}$ is the tensor form of the quadrupole term.

The interaction Hamiltonian between systems A and B, $V_{AB}(R)$, can now be written as follows:

$$V_{AB}(R) = \frac{Z_A\, Z_B}{R} + \frac{(Z_B\, M_A - Z_A\, M_B) \cdot R_o}{R^2} + \frac{M_A \cdot M_B - 3(M_A \cdot R_o)\,(M_B \cdot R_o)}{R^3}$$

$$+ \frac{R_o(Z_A\, D_B + Z_B\, D_A) \cdot R_o}{2R^3} + \text{higher terms} \qquad (3)$$

In the first approximation, each term in equation (3) is zero. In the second approximation, the first non-zero term is the dipole-dipole interaction term, i.e.

$$\frac{M_A \cdot M_B - 3(M_A \cdot R_o)\,(M_B \cdot R_o)}{R^3}$$

The interaction energy in the second order approximation, which is proportional to the square of the interaction Hamiltonian, can now be written as follows:

$$U_{AB}(R) = \frac{C_I}{R^6} + \frac{C_{II}}{R^8} + \frac{C_{III}}{R^{10}} + \tag{4}$$

where C_I, C_{II}, and C_{III} are constants.

Since the dipole-dipole term decreases least rapidly with R, this will be the dominant term in $U_{AB}(R)$. We can thus approximate,(*) $U_{AB}(R)$ as follows:

$$U_{AB}(R) = \frac{C_I}{R^6} = -\frac{C_6}{R^6} = -\frac{C_{AB}}{R^6} \tag{5}$$

(A negative sign has been chosen, since the correction in the second approximation to the lowest eigenvalue is always negative.)

From equation (5), it is obvious that for two neutral systems in S states, the binding energy in the second approximation varies as R^{-6}. This binding is called Van der Waal's force and constitutes the dominant term in the long range forces between neutral systems. The force constant, C_{AB}, depends upon the state of the two systems and their mutual orientation. A classical calculation of C_{AB} is not feasible because of lack of precise knowledge of the dipole terms in equation (3). A quantum mechanical treatment of the interaction will now be described.

(B) Quantum Mechanical Theory of Interaction

Attention in the following discussion will be confined to the leading term in the interaction energy. The first quantum mechanical treatment of the dipole-dipole interactions in terms of the wavefunction describing the interacting systems was given by London (ref. 2a). His method was essentially a form of ordinary perturbation theory which will now be applied to calculate the interaction constant, C_{AB}.

According to the widely used perturbation theory (ref. 3), the perturbed Hamiltonian of an atomic system is written as $(H_o + H')$ whereas the eigenvalues and eigenfunctions of the perturbed system may be written as follows:

$$E = \sum_{n=0}^{\infty} E_n; \quad \Psi = \sum_{n=0}^{\infty} \Psi_n \tag{6}$$

(*)It must, however, be pointed out that in cases involving one negative ion and one neutral atom (such as $H^- - H$), R^{-8} term may be of considerable importance in low energy scattering.

The Schroedinger equation describing the system for non-zero perturbation is:

$$(H_o + H' - E)\,\Psi = 0 \tag{7}$$

For any two atoms in nondegenerate spherically symmetrical ground states, the second order change in energy, which is equivalent to $\frac{C_{AB}}{R^6}$, can be written as follows:

$$\frac{C_{AB}}{R^6} = S' \frac{|H'_{on}|^2}{E_o - E_n} \tag{8}$$

where summation S' extends over all states other than the ground state.

For an (H - H) system;

$$\frac{C_{AB}}{R^6} = -\,6.499\ e^2 a_o^5/R^6 \tag{9}$$

For (He-He) system;

$$\frac{C_{AB}}{R^6} = -\,1.47\ e^2 a_o^5/R^6 \tag{10}$$

The variational technique gives the following values for the long range interaction.

(H - H) system (ref. 4);

$$\frac{C_{AB}}{R^6} = -\,6.499026\ e^2 a_o^5/R^6 \tag{11}$$

(He-He) system (ref. 4a);

$$\frac{C_{AB}}{R^6} = -\,1.459\ e^2 a_o^5/R^6 \tag{12}$$

The most widely accepted values for $\frac{C_{AB}}{R^6}$ for the two systems are as follows:

$$\left.\begin{array}{ll} \text{(H - H) system:} & -6.499\ e^2 a_o^5/R^6 \\ \text{(He-He) system:} & 1.473\ e^2 a_o^5/R^6 \end{array}\right\}\ \text{ref. 4b}$$

Both the perturbation theory and the variational principle require a knowledge of the atomic wavefunctions. However, this is possible only in the case of simple one-electron and two-electron systems. Consequently, a number of alternative techniques of experimentally measuring the interaction constant have been developed over the years. Some of the prominent techniques are described below:

I. Methods based on oscillator strength determinations

II. Methods based on multipole polarizability measurements

III. Empirical methods

I. Oscillator Strength Methods

Dalgarno (ref. 5) has expressed van der Waals' interaction in terms of experimentally measurable oscillator strengths. His expression is as follows:

$$\frac{C_{AB}}{R^6} = \frac{3}{2R^6} \sum_m \sum_{n \neq 0} \frac{f_m^A \, f_n^B}{(E_o^A - E_m^A)\,(E_o^B - E_n^B)\,(E_o^A - E_m^A + E_o^B - E_n^B)} \tag{13}$$

where f_m^A and f_n^B are electric dipole oscillator strengths(*) defined as follows:

$$f_m^A = 2/3\,(E_m^A - E_o^A)\,|\phi_o^A, \textstyle\sum_i r_A^i\, \phi_m^A|^2$$

$$f_n^B = 2/3\,(E_n^B - E_o^B)\,|\Psi_o, \textstyle\sum_j r_B^j\, \Psi_n^B|^2$$

where r_A^i and r_B^j are the position vectors of the interacting electrons.

(*)In the central field model, the oscillator strength for a single electron transition between (n, ℓ) and $(n', \ell \pm 1)$ states is defined as follows:

$$f_{n,\ell}^{n',\ \ell \pm 1} = 1/3 \left(\frac{\ell_{max}}{2\ell + 1}\right) (E'_{n',\ \ell \pm 1} - E_{n,\ell})\, |M_{n,\ell}^{n',\ \ell \pm 1}|^2 \tag{14}$$

where $\ell_{max} = \ell$ for $\ell \to \ell - 1$
$= \ell + 1$ for $\ell \to \ell + 1$

and $|M_{n,\ell}^{n',\ \ell \pm 1}|$ = bound-bound matrix element for the transition

The oscillator strengths can be extended to include transitions into the continuum where the matrix element takes the following form:

$|M_{n,\ \ell}^{E,\ \ell \pm 1}|$ = bound-free matrix element

where E = binding energy of the (n, ℓ) electron.

E, ϕ, and Ψ are the appropriate eigenvalues and eigenfunctions. One feature of Van der Waals forces is at once apparent from equation (13). Suppose E_o^A and E_o^B are the normal states of atoms A and B. Both f-values are then positive, $E_m^A > E_o^A$ and $E_n^B > E_o^B$. Clearly $\frac{C_{AB}}{R^6}$ is then negative. Hence the general theorem regarding dispersion forces: Atoms (molecules) in their normal states attract each other.

A theoretical calculation of oscillator strengths will require a knowledge of the appropriate wavefunctions and has been possible only in the simple hydrogen-like systems. However, oscillator strengths are related to a number of experimentally measurable parameters (see below) which can be used to calculate them. Furthermore, the existing experimental values in conjunction with oscillator strength Sum Rules (ref. 6) can be used to obtain additional oscillator strength values.

An alternative, and more convenient, method of evaluating sums like equation (13) has been proposed by Bell (ref. 5a). This method does not require a detailed knowledge of individual f_m^A values, but enables one to compute equation (13) directly from selected oscillator strength sums. (Some of these sums may be deduced directly from refractive index and Verdet constant measurements.)

Some of the experimental techniques for measuring electric dipole oscillator strengths are described below.

(a) Lamb Shift

The energy separation between the 2 $S_{\frac{1}{2}}$ and 2 $P_{\frac{1}{2}}$ states in hydrogen and helium atoms is related to the relevant oscillator strengths. According to Bethe (ref. 7), the Lamb shift is related to dipole oscillator strength in the following manner.

$$\ln k_o = \frac{\sum_n f_n (E_o - E_n)^2 \ln (E_o - E_n)}{\sum_n f_n (E_o - E_n)^2} \tag{15}$$

where k_o is the appropriate Lamb shift and other terms have been defined above.

Thus a determination of k_o, should enable one to calculate f_n. A direct measurement of Lamb shift for an atom also permits a calculation of the mean atomic excitation potential as indicated in (b) below.

(b) Stopping Power for Charged Particles

The penetration of a beam of charged particles into matter is characterized by two mean excitation energies, I and I', associated with the

stopping power and straggling, respectively. According to Fano (ref. 8), these quantities are related to the electric dipole oscillator strengths, f, in the following manner.

$$\ln I = \frac{S'_n f_n \ln (E_n - E_o)}{S'_n f_n} \tag{16}$$

$$\ln I' = \frac{S'_n f_n (E_n - E_o) \ln (E_n - E_o)}{S'_n f_n (E_n - E_o)} \tag{17}$$

where the summation, S'_n, includes integration over the continum but excludes n = 0 term. Thus an experimental determination of I and I' should provide information on f_n and vice versa.

(c) Refractive Index of a Gas

According to optical dispersion theory (ref. 9), the frequency-dependent refractive index, n, of an isotropic dielectric medium can be written as follows:

$$n^2 = (n_o + i\beta)^2 = 1 + \frac{Ne^2}{m} \sum_j \left(\frac{f_j}{\omega_j^2 - \omega^2 - i\,\gamma_j\,\omega} \right) \tag{18}$$

where γ_j is the damping constant associated with frequency ω_j and

N = number of electrons/cc

ω_j = resonant frequency of the bound electrons.

Thus an experimental measurement of the refractive index of a gas at a number of frequencies gives information about its appropriate atomic oscillator strengths and hence the long range interaction constant, C_{AB}. Bell (ref. 5a) has discussed calculation of Van der Waals force constants for several pairs of atoms from their oscillator strength sums, each of which can be derived from experimentally determined refractive index values.

II. Multipole Polarizability Methods

Another important measurable quantity that is often used in calculating C_{AB} is the polarizability of the atom. The dynamic polarizability $\alpha(\nu)$

of a physical system,(*) having instantaneous dipole moment M, due to electrical waves of frequency ν and electric veclor along X is given by

$$\alpha_x(\nu) = 2e^2 \sum_n \frac{|(n|X|o)|^2 [E(n) - E(o)]}{[E(n) - E(o)]^2 - (h\nu)^2} \tag{19}$$

where $(n|X|o)$ is the matrix element of the transition $n \to 0$ and $E(n)$ and $E(o)$ are the energies of states n and o, respectively.

The fact that polarizabilities are difficult to calculate need not disturb us for the values of α may be taken from the experiment or may be expressed in some other computationally convenient way (see below). London (ref. 26) established the following relationship between the force constant, C_{AB}, and the polarizability, α, of the interacting systems.

$$C_{AB} = \frac{3}{2} \frac{I_A I_B}{I_A + I_B} \alpha_A \alpha_B \tag{21}$$

where I's are the ionization potentials(**) and α's are the electric dipole polarizabilities of the interacting atoms.

Approximate estimates of $\alpha(\nu)$ can be made using Pade approximants (ref. 12) and variational techniques (ref. 13). As an alternative to purely theoretical calculations, one can obtain these values from optical dispersion data and oscillator strength Sum Rules. Two important techniques of experimentally measuring polarizability are indicated below.

(a) Refractive Index of Gases

The refractive index n of a gas of number density N can be obtained from the Lorentz-Lorenz formula as follows:

$$3 \frac{n^2 - 1}{n^2 + 1} = 4 \pi N \alpha(\nu)$$

(*)The static polarizability, according to (19) takes the form:

$$\alpha_x(0) = 2e^2 \sum_n \left\{ |(n|X|o)|^2 \Big/ E(n) - E(o) \right\} \tag{20}$$

(**)Identification of I with the ionization potential often leads to poor results (ref. 10 and ref. 11).

For a case (gases) when $n \approx 1$, we can modify (22) as follows:

$$3 \frac{(n + 1)(n - 1)}{3} = 4 \pi N \alpha(\nu)$$

or

$$(n - 1) = 2 \pi N \alpha(\nu) \tag{23}$$

Thus a measurement of n will enable a determination of $\alpha(\nu)$. (Also a measurement of n and an independent determination of $\alpha(\nu)$ is expected to give information on the number density and hence the pressure of the gas.)

(b) Rayleigh Scattering Cross Section

The scattering cross section of a gas for incident natural light is related to the refractive index and hence polarizability of the atom/molecule of the gas in the following manner (ref. 14).

$$\sigma(\lambda) = \frac{8 \pi^3}{3 \lambda^4} \left(\frac{n^2 - 1}{N}\right)^2 \tag{24}$$

where N = Loschmidt number.

Thus a measurement of $\sigma(\lambda)$ will permit a determination of n, which can be used to calculate $\alpha(\nu)$ using equations (22) and (23).

III. Empirical Methods

(a) Thermal Molecular Beam Scattering.- As has been shown by Landau and Lifshitz (ref. 14a), the total elastic scattering cross section of low energy atoms/molecules from a potential of the form $\frac{C}{R^6}$ is given by:

$$\sigma_{el.sc}(v) = \text{Const} \left(\frac{C}{\hbar v}\right)^{2/5} \tag{25a}$$

where v is the relative velocity of the colliding atoms/molecules. Thus a measurement of $\sigma_{el.sc}$ at several energies can be used to calculate C_{AB} for selected atom-molecule systems.(*) Several such measurements have been

(*)Since the experimental scattering cross section is obtained from the measured incident and scattered beam intensities, a measurement of $\sigma_{el.sc}$ also enables a computation of the number density of the scattering gas. (This information, coupled with the temperature of the scattering gas, should enable calculation of the scattering gas pressure.)

reported for atom-atom and atom-molecule systems. The latest measured and the calculated values of C_{AB} are in excellent agreement (ref. 14b). The C_{AB} values may also be calculated from measurements of diffrential scattering cross section at small angles.

(b) Lennard-Jones Potential.- An important empirical expression(*) widely used in the case of nonpolar atoms/molecules is the Lennard-Jones potential given below.

$$U(R) = 4\ \varepsilon \left\{ \left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6} \right\} \tag{25b}$$

where σ is an adjustable parameter.

The $\left(4\ \varepsilon\ \frac{\sigma^{12}}{R^{12}}\right)$ term gives an approximation to the short range repulsion interaction whereas the $\left(-4\ \varepsilon\ \frac{\sigma^{6}}{R^{6}}\right)$ is the familiar dispersion interaction. This expression will not be discussed any further in this report.

Summary of Experimental Parameters Used for Calculating Long Range Forces

Using the above techniques, the values of dipole polarizabilities, electrical dipole oscillator strength and C_{AB} have been calculated by a number of workers. Some representative results are summarized in tables I, II, and III and IV below.

(*)See "Molecular Theory of Gases and Liquids" by Herschfelder, Curtiss, and Bird (published by John Wiley and Sons, 1954).

Table I.- Dipole Polarizabilities of Various Atoms and Ions

Atom (or ion)	α, Dipole Polarizability in Units(*) of $(a_o)^3$	
He	1.38	Ref. 13
Li^+	0.19	Ref. 13
H^-	174.20	Ref. 13
H	4.20 †	LRC
H_2	5.9 †	LRC
Li	165	Ref. 5
Na	166	Ref. 5
K	281	Ref. 5
Rb	296	Ref. 5
Cs	363	Ref. 5

(*) $a_o = 0.53 \times 10^{-8}$ cm.

(†) Calculated from London's formula, $C_{AB} = \frac{3}{2} \frac{I_A I_B}{I_A + I_B} \alpha_A \alpha_B$

In the case of hydrogen molecule, the ionization potential has been assumed to be same as for a hydrogen atom. If we assume the ionization potential of the H_2 molecule to be 15.6 eV, the dipole polarizability for the H_2 molecule is calculated to be 5.49 $(a_o)^3$.

Table II.- Oscillator Strengths for Resonance Transitions in Various Alkali Metals

Alkali Metal	f, Oscillator Strengths (Experimental)	
Li	0.75	Ref. 15
Na	0.98	Ref. 16
K	0.99	Ref. 16
Rb	1.00	Ref. 16
Cs	0.98	Ref. 17

Dalgarno (ref. 5) used these values of oscillator strengths to calculate the polarizability by using the following relation:

$$\alpha = \sum_n{}' \frac{f_n}{(E_o - E_n)^2} = S_n{}' \frac{f_n}{(E_o - E_n)^2}$$

The values thus calculated have been summarized in table I.

Table III(a).- Values of C_{AB} for Hydrogen and Inert Gases (refs. 18 and 19)

A \ B	C_{AB} (in atomic units)(*)				
	H	H_2	He	Ne	A
H	6.50	9.24	2.82	5.67	20.15
H_2	9.24	13.30	4.21	8.56	29.60
He	2.82	4.21	1.46	3.07	9.88
Ne	5.67	8.56	3.07	6.63	20.63
A	20.15	29.60	9.88	20.63	68.08

(*)One atomic unit $= e^2 a_o^5 = 9.63 \times 10^{-61}$ erg-cm^6 $= 6.02 \times 10^{-49}$ electron volt-cm^6.

Table III(b).- Values of C_{AA} for Alkali Metals (refs. 5, 15a)

Metals	Li	Na	K	Rb	Cs
C_{AA}, in atomic units (theoretical)[5]	1.4×10^3	1.6×10^3	3.5×10^3	3.8×10^3	5.2×10^3
C_{AA}, in atomic units (experimental)[15a]	—	0.92×10^3	1.59×10^3	1.67×10^3	3.46×10^3

Table III(c).- Values of C_{AB} for Alkali Metals and Inert Gases (ref. 5)

C_{AB} in Atomic Units								
A \ B	He		Ne		A		Kr	Xe
	Exp	Theory	Exp	Theory	Exp	Theory	Theory	Theory
Li	15	22	20	48	200	200	300	480
Na	19	25	42	52	200	210	330	530
K	33	33	53	68	370	280	420	680
Rb	27	34	51	69	260	280	430	700
Cs	31 (390)*	38	59	77	250	320	480	780

(*)This value has been derived from the measurements of Easterman et al. (ref. 20).

Table III(d).- Values of C_{AB} Calculated by Using the Combination Rule $C_{AB} = (C_{AA}C_{BB})^{1/2}$ (also shown are directly calculated values).

System	C_{AB} (Calculated) in atomic units	C_{AB} (from Table III(c)) in atomic units
He - Li	45.2	22
He - Na	48.3	25
He - K	71.5	33
He - Rb	74.5	34
He - Cs	87.1	38

This table clearly indicates that the approximation $C_{AB} = (C_{AA}C_{BB})^{1/2}$ overestimates the van de Waals' force constant for inert gas-alkali metal system by about a factor of 2.

Table IV.- Values of C_{AB} for H_2 Molecule and Alkali Metals

System	C_{AB} in atomic units (ref. 19)
H_2-Li	87.6
H_2-Na	96.3
H_2-K	128.0
H_2-Rb	132.0
H_2-Cs	148.0

Gaseous Adsorption on Metallic Surfaces

Another important area where long range forces play an important role is gaseous adsorption on metallic surfaces. When neutral gaseous molecules are adsorbed on metallic surfaces, there are two distinctly different types of forces in play: The unsaturated valence forces leading to chemisorption and the dispersion forces leading to physical adsorption. The chemisorption sets in strongly at higher temperatures while physical adsorption (van der Waal's adsorption) is predominant at low temperatures. We will confine our remarks only to physical adsorption.

When a visitor atom is adsorbed on a metal surface, the following forces will come into play: (1) The dispersional force arising from the interaction between the instantaneous dipole of the adsorbed atom (adatom) and the metallic atoms; (2) the exchange force resulting from the exchange of electrons in the atom and the metal conduction band electrons (this is a repulsive force); (3) the ionic interaction(*) resulting from the electron transfer to the metal. Thus the total energy of interaction, E, between the adatom/molecule and the metal atoms can be written as follows:

$$E = E\ (\text{dispersion}) + E' \tag{26}$$

(*)Most of the earlier treatments of the ionic interaction ignore the electronic structure of the metal (refs. 21 and 22). Recently Wojciechowski (ref. 23), however, has included the atomic structure of the metal surface in the calculation of the adatom-metal ionic interaction.

where $E' = E\ (\text{exchange}) + E\ (\text{ionic})$ (26a)

$$\simeq E\ (\text{exchange}) \tag{26b}$$

This is justifiable since the percentage of ionization of the adsorbing gases considered in the present calculations (He and H_2) is not expected to be very high at the temperatures where physical adsorption phenomenon occurs. If, however, the charge transfer from an adsorbed species to the metallic substrate does occur (as would be the case for alkali adatoms on metallic surfaces, for instance), the ionic effects can be quite large. Bennett and Falicov (ref. 24a), being most concerned with such charge transfer and Pauli exclusion principle, developed a self-consistent field method for evaluating the energy of adsorption and the amount of charge transferred using a 1 electron model of the metal. They neglected all dispersional effects and assumed the action of an image force for the charge transfer problem. Good agreement with experimental results was obtained for K, Rb, and Cs adsorption on tungsten substrate despite the omission of dispersional effects. This indicates that if ionic forces do exist, they usually dominate intermolecular effects. This, however, is not expected to be the case with helium gas or H_2 gas. The former is a closed shell atom, whereas in the latter case, a molecule of H_2 may become adsorbed on the metal surface and then dissociate into two adsorbed H-atoms. These adsorbed atoms may subsequently diffuse into the metal lattice forming a solid solution (metal hydride). The dissociation energy (24b) of H_2 molecule is $(36104 \pm 105)\text{cm}^{-1}$, thus making it a very unlikely process at low temperatures where physical adsorption occurs.

Thus we have,

$$E \approx E\ (\text{dispersion}) + E\ (\text{exchange}) \tag{27}$$

Pollard (ref. 24) has treated the exchange part of the mutual energy of an adsorbed neutral atom/molecule on a metal surface. Following a similar technique, we have calculated E (exchange) for hydrogen and helium gases adsorbed on several metallic surfaces (see appendix 2). The results are summarized in table V. During these calculations, it became apparent that the metals with larger characteristic radius, defined as the radius of a sphere containing one atom of the metal, have lower values of heat of adsorption, mainly due to increased equilibrium inter-atomic separation.

CONCLUSIONS

Various theoretical and experimental techniques for measuring the long range force constant between neutral atomic systems have been reviewed. Typical results for some commonly occurring gas-metal combinations have been summarized. During the course of discussion of various calculational techniques, new methods of measuring several gaseous properties have been indicated. For instance, an accurate measurement of Lamb shift in an atom should provide information on the stopping power of the gas atoms for charged particles. The measurement of refractive index of a gas can be used to

obtain the pressure of the gas and similarly, the total elastic scattering cross section in atomic beam measurements is expected to provide an accurate measure of the number density of the scattering gas. In the case of physical adsorption, the important role of exchange forces between the adatom electrons and the conduction band electrons has been demonstrated. It has been found that the heat of physical adsorption is small for metals with large values of characteristic radii.

Table V.- Values of E(binding) = E(dispersion) + E(exchange) for Hydrogen and Helium Adsorbed on Several Alkali Surfaces

No.	System	E(dispersion) at 10^{-8} cm for single atom (molecule)-atom from Table III(c) and IV	E(disp) at 10^{-8} cm integrated over entire metal (see note 2)	$E(disp)_{min}$ integrated over entire metal surface	E(exchange) corresponding to $E(disp)_{min}$ integrated over entire metal	E(binding) over entire surface of metal
1	He + Lithium	(-) 13.15 ev	(-) 0.255 ev	(-) 0.0137 ev	(+) 0.0044 ev	(-) 0.0093 ev
2	He + Sodium	(-) 15.93 ev	(-) 0.220 ev	(-) 0.0071 ev	(+) 0.0022 3v	(-) 0.0049 ev
3	He + Potassium	(-) 18.04 ev	(-) 0.1800 ev	(-) 0.0033 ev	(+) 0.0007 ev	(-) 0.0026 ev
4	He + Rubidium	(-) 20.25 ev	(-) 0.165 ev	(-) 0.0024 ev	(+) 0.0002 ev	(-) 0.0022 ev
5	He + Cesium	(-) 22.64 ev	(-) 0.150 ev	(-) 0.0018 ev	(+) 0.0002 ev	(-) 0.0016 ev
6	H_2 + Lithium	(-) 51.47 ev	(-) 0.870 ev	(-) 0.0340 ev	(+) 0.0120 ev	(-) 0.0220 ev

Table V (Cont.)

No.	System	E(dispersion) at 10^{-8} cm for single atom (molecule)-atom from Table III(c) and IV	E(disp) at 10^{-8} cm integrated over entire metal (see note 2)	$E(disp)_{min}$ integarted over entire metal surface	E(exchange) corresponding to $E(disp)_{min}$ integrated over entire metal	E(binding) over entire surface of metal
7	H_2 + Sodium	(-) 57.80 ev	(-) 0.770 ev	(-) 0.0190 ev	(+) 0.0055 ev	(-) 0.0135 ev
8	H_2 + Potasium	(-) 76.77 ev	(-) 0.675 ev	(-) 0.0100 ev	(+) 0.0020 ev	(-) 0.0080 ev
9	H_2 + Rubidium	(-) 79.20 ev	(-) 0.630 ev	(-) 0.0078	(+) 0.0016 ev	(-) 0.0062 ev
10	H_2 + Cesium	(-) 88.80 ev	(-) 0.580	(-) 0.0058 ev	(+) 0.0010 ev	(-) 0.0048 ev

Notes: (1) The binding energies are expressed in terms of electron volts. In order to obtain the Heats of Adsorption in units of calories/mole, use the following conversion factor:

0.17 ev/molecule = 4000 cals/mole

(2) The values listed in the fourth column have been calculated using the formalism developed by Margenau and Kestner in their recent book entitled "Theory of Intermolecular Forces" (published by Pergamon Press, New York, 1971).

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APPENDIX I

1. Atom-Molecule Long Range Forces

The calculation of dispersion forces in this case is slightly more complicated than for an atom-atom case, mainly, because of the anisotrophy of the molecular polarizability. The dipole-dipole interaction potential can be written (ref. 20) in the following form:

$$U_{AB}(R) = -\frac{C}{R^6}\left(1 + \frac{A_{disp}}{2}(3\cos^2\theta - 1)\right)$$

$$U_{AB}(R) = -\frac{C}{R^6}\left[1 + A_{disp}\, P_2(\cos\theta)\right] \qquad \text{(A-1)}$$

where $P_2(\cos\theta)$ is the Legendre polynomial of the second order and θ is the angle between R and the plane of molecular rotation and $A(disp)$ is defined below.

$A(disp)$ = anisotropy factor for the dispersion potential

$$= \frac{\alpha^{11} - \alpha^{\perp}}{\alpha^{11} + 2\alpha^{\perp}}$$

where α^{11} and $\alpha^{\perp}$ stand for the polarizability of the molecule parallel and perpendicular to the molecular axis, respectively.

Quadrupole-dipole induction effects may further complicate the atom-molecule long range interaction calculations.

2. Molecule-Molecule Long Range Forces

In this case, in addition to the angular dependence of polarizability and the induction effects, one must also include electrostatic interactions between the two molecules. Thus the interaction energy becomes:

$$U_{AB}(R) = U(\text{dispersion}) + U(\text{induction}) + U(\text{electrostatic})$$

The induction effect has been calculated by Margenau (ref. 26). The electrostatic term may be written (ref. 27) as follows:

$$U_{AB}(\text{electrostatic}) = \frac{M_1 M_2}{R^3} B(1,2) + \left[\frac{M_1 Q_2}{R^4} B(1,2) + \frac{M_2 Q_1}{R^4} B(2,1)\right]$$

$$+ \left[\frac{Q_1 Q_2}{R^5} B(1,2) + \frac{M_1 O_2}{R^5} B(1,2) + \frac{M_2 O_1}{R^5} B(2,1)\right]$$

$$+ \text{higher terms} \qquad \text{(A-2)}$$

where M, Q, and O have their usual significance and B(A,B) are the angular functions of the two molecules.

APPENDIX II

CALCULATION OF HEATS OF PHYSICAL ADSORPTION BETWEEN NEUTRAL GASEOUS MOLECULES AND A METAL SURFACE

At short distances, the interaction energy between visitor atoms/molecules and the metal atoms is comprised of two parts: (1) Attractive van der Waals interaction and (2) short range exchange forces arising from the overlap of electron clouds. In order to obtain the total potential energy of the system, the potential of the attractive forces must be added(*) to the exchange term. On adding the exchange potential with the van der Waals potential, one obtains potential functions possessing characteristic minima. The depth of these minima determine the binding energy of the adatom and their position gives the equilibrium separation of the adatom from the metal surface. The values of these parameters for H_2 and He gas in contact with several metals have been calculated by Pollard (ref. 24). Using similar techniques, we have calculated equilibrium separation distances and the corresponding binding energies for H_2 and He gas and several alkali metals. According to these techniques, the visiting atom is represented by a core of charge +e above the surface at a point r_A and an electron with the position coordinate r_a. The solid is represented by atomic cores of charge $Z_J e$ at points r_J together with electrons at points r_j. The wavefunction for the whole solid-atom system is taken to be:

$$\Psi = C_+ \Psi_1 + C_- \Psi_2 \tag{A-3}$$

where C_+ and C_- depend on the spin function of the electron in the visiting atom. The <u>total</u> energy of the system is given by:

$$E = \frac{\int \Psi^* H \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau} \tag{A-4}$$

(*)The addition of first order exchange forces to the second order dispersion terms may not cause great error if the exchange forces are small at the equilibrium distance between the adatom and the metal surface. This, indeed, is the situation in the cases considered here.

where

$$H = -\frac{\hbar^2}{2m}\nabla_a^2 - \frac{h^2}{2m}\sum_j \nabla_j^2 + \frac{1}{2}\sum_{J,L}{}' \frac{Z_J\, Z_L\, e^2}{r_{JL}} + \sum_L \frac{e^2}{r_{AL}}$$

$$- \sum_{J,k} \frac{Z_J\, e^2}{r_{Jk}} - \sum_J \frac{Z_J\, e^2}{r_{Ja}} - \sum_k \frac{e^2}{r_{Ak}} - \frac{e^2}{r_{Aa}}$$

$$+ \frac{1}{2}\sum_{jk}{}' \frac{e^2}{r_{jk}} + \sum_j \frac{e^2}{r_{aj}} \qquad \text{(A-5)}$$

The exchange terms refer only to those electrons in the solid having the same spin as that of the electron in the visiting atom. The <u>exchange interaction</u>, $A(\rho_s, D_m)$, is given by:

$$A(\rho_s, D_m) = \frac{e^2 \left[p(\rho_s)\, G(D_m) + q(\rho_s) \left\{ p(\rho_s) - 1 \right\} F(D_m) \right]}{\left[1 - p(\rho_s)\, F(D_m) \right]} \qquad \text{(A-6)}$$

where

$$F(D_m) = \frac{1}{2}\left(1 + \frac{D_m}{a}\right) e^{-\frac{2\, D_m}{a}}$$

$$G(D_m) = \left(\frac{1}{2a}\right) e^{-\frac{2\, D_m}{a}}$$

$$p(\rho_s) = 3\left[\left(\frac{\rho_s}{a}\right) \operatorname{Cosh}\left(\frac{\rho_s}{a}\right) - \operatorname{Sinh}\left(\frac{\rho_s}{a}\right)\right] \Big/ \left(\frac{\rho_s}{a}\right)^3$$

$$q(\rho_s) = \left(\frac{3}{a}\right)\left[\text{Cosh}\left(\frac{\rho_s}{a}\right) - 1\right] \Big/ \left(\frac{\rho_s}{a}\right)^3$$

ρ_s = radius of sphere of volume $\frac{V}{n}$ containing one metal electron of a given spin

$= 2^{1/3}\, r_s$, where r_s is the characteristic radius of the metal.

r_s = characteristic radius of the metal

$$= \left[\frac{3}{4\pi}\left[\frac{\text{gm. at. weight of metal}}{\text{(Av. No.) (Density of metal)}}\right]\right]^{1/3}$$

D_m = equilibrium distance of the adatom from the metal surface. Its numerical value is obtained from (D_m/ρ_s vs r_s) values tabulated by Pollard (ref. 24).

$a(He) = 0.62a_o$

$a(H_2) = 0.95a_o$

The total exchange interaction of both electrons in He and H_2 will be twice that for one of them when the metal contains equal numbers of both spin varieties and when the distance from the metal is large enough to make double exchange integral negligible as is the case for VDW forces.

The various results are summarized in Tables VI to VIII.

Table VI.- Summary of Equilibrium Separation Distances Between Adatom or Admolecule and Metal Surfaces

Metal \ Adsorbed Gas Atom or Molecule	H_2	He
Li	2.94×10^{-8} cm	2.65×10^{-8} cm
Na	3.44×10^{-8} cm	3.24×10^{-8} cm
K	4.08×10^{-8} cm	3.80×10^{-8} cm
Rb	4.32×10^{-8} cm	4.08×10^{-8} cm
Cs	4.64×10^{-8} cm	4.40×10^{-8} cm

Table VII.- Summary of Exchange Interaction Energies Between the Adatom or Admolecule and the Metal Surface

Metal \ Metal gas atom or molecule	H_2	He
Li	(+) 0.0120 ev	(+) 0.0044 ev
Na	(+) 0.0020 ev	(+) 0.0022 ev
K	(+) 0.0020 ev	(+) 0.0007 ev
Rb	(+) 0.0016 ev	(+) 0.0002 ev
Cs	(+) 0.0010 ev	(+) 0.0002 ev

Table VII.- Summary of the Binding Energies Corresponding to the Equilibrium Separation Distances Between the Adatom or Admolecule and the Metal Surfaces

Metal \ Adsorbed Gas Atom or Molecule	H_2	He
Li	(-) 0.0220 ev	(-) 0.0093 ev
Na	(-) 0.0135 ev	(-) 0.0049 ev
K	(-) 0.0080 ev	(-) 0.0026 ev
Rb	(-) 0.0062 ev	(-) 0.0022 ev
Cs	(-) 0.0048 ev	(-) 0.0016 ev

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15. Supplementary Notes

A discussion of various calculational techniques for determining long range force constant between neutral atomic systems has indicated several new methods for measuring gaseous properties.

16. Abstract

A discussion of various theoretical and experimental techniques for the calculation of long range interaction between two atomic systems at moderate separation is presented. Some applications of these techniques for obtaining gaseous properties are described. The forces between neutral molecules and metallic surfaces have also been discussed and numerical values of heats of adsorption for a number of systems have been calculated.

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