The Forces Between Neutral Molecules and Metallic Surfaces

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(Received May 23, 1941)

A general formula is developed for the interaction between a neutral molecule and a metal, and its relation to the image force law is exhibited, (Section III). The latter is shown to be valid only for molecules containing slowly moving charges, such as rigid permanent dipoles. A fairly accurate evaluation of the general formula involving empirical polarizabilities, f values, and resonance frequencies is made in Section IV. The numerical values for a number of gases and metals are collected in Tables I and II.

I. INTRODUCTION

EXAMINATION of the rapidly growing experimental[1] material dealing with the adsorption of gases on metallic surfaces has brought into evidence the action of two types of forces which cause neutral molecules to be attracted to metals: unsaturated valences and van der Waals interactions. The former produce the phenomena often referred to as *chemisorption*, the latter give rise to what is now commonly called *physical* or *van der Waals* adsorption. The two types occur generally in different ranges of temperature; physical adsorption is usually predominant at low, while chemisorption sets in strongly at high, temperatures, a fact which is most easily explained by supposing that chemisorption requires activation but physical adsorption does not. (For this reason chemisorption is sometimes called "activated adsorption.") The energy liberated by physical adsorption is much smaller than that evolved in chemisorption; the values of the heats of adsorption for the former type are in the neighborhood of 4000 cal./mole (=0.17 electron volt/molecule) while the latter leads to values between 10,000 and 200,000 cal./mole.

The distinction here discussed is best clarified, perhaps, by reference to a typical graph (Fig. 1) in which the volume of gas adsorbed on a metal surface is plotted against the temperature at which adsorption occurs. At low temperatures, van der Waals forces attract a large amount of gas to the surface. Because of the weak binding produced by these forces, these molecules are easily driven off when the temperature rises. But at sufficiently high temperatures the chemical forces, which come into play only when the kinetic energy of the molecules is great enough to supply the heat of activation, cause larger volumes of gas to be occluded to the metal. These, in turn, are released at very high temperatures when the kinetic energy of the molecules becomes comparable with the heats of chemisorption.

Accessory features, such as the phenomenon of surface catalysis and the dependence of heats on the nature of the crystal face, complicate the problem of chemisorption. Even aside from these, a detailed calculation of the attractive valence forces between the gas molecules and the metal surface is hardly feasible at present and will not be undertaken here. The van der Waals forces, on the other hand, are amenable to reasonably accurate treatment; they are the object of the present study. Attention will be given only to the attractive part of these forces, operative at distances of separation greater than the diameter of the molecules. And even here, only the long range constituent proportional to D^{-7} (dipole-dipole force) will be considered. In a subsequent paper by one of us[2] a composition of the attractive van der Waals with the re-

[1] For a summary of experimental work see: N. K. Adams, *The Physics and Chemistry of Surfaces*, second edition (Oxford University Press, 1938), *The Adsorption of Gases by Solids* (The Faraday Society, 1932); also in Trans. Faraday Soc. **28**, 131–447 (1932); J. K. Roberts, *Some Problems in Adsorption* (Cambridge Physical Tracts No. 7, 1939).

[2] W. G. Pollard, to be submitted.

pulsive exchange forces will be undertaken, a procedure which leads to a numerical evaluation of the minimum potential energy thus created and hence to an estimate of the heats of van der Waals adsorption.

One of the first attacks upon the problem was made by Lennard-Jones[3] who calculated the interaction between a molecule and a metal by the image method, a procedure which implies that the electrons in the molecule create images of opposite charge within the metal and that these images move in definite phase relations with the molecular charges. The result obtained for the potential energy of interaction has the simple form

$$W = -e^2\langle R^2\rangle_{\mathrm{Av}}/12D_0^3 \qquad (1)$$

where $\langle R^2\rangle_{\mathrm{Av}}$ is the mean square displacement of all electrons in the molecule and D_0 the distance of the molecule from the metal surface. Specific properties of the metal do not enter into the formula because all metals are assumed to be perfect conductors.

There is, of course, an obvious criticism of the assumptions leading to (1). The electrons in the metal can adjust themselves to form images of static or slowly moving external charges, but because of their finite relaxation time they are incapable of simulating the very rapid motions of the instantaneous dipoles composing a non-polar molecule. In fact while a metal is a reasonably perfect conductor with respect to alternating fields of low frequencies, it takes on the properties of non-conductors at frequencies not far beyond the visible range, and this happens in a manner peculiar to each metal. Now the molecules and atoms whose heats of adsorption have been investigated, particularly the rare gases, have resonance frequencies far in the ultraviolet, so that one would expect a metal to behave in these interactions not so much like a perfect conductor characterized by image forces, but more like an insulator. We note in this connection that the method of London[4] for computing heats of adsorption of non-conductors, which takes no account whatever of the presence of free electrons, yields even for metals numerical values that are comparable with experimental data.

[3] J. E. Lennard-Jones, Trans. Faraday Soc. **28**, 334 (1932).
[4] F. London, Zeits. f. physik. Chemie, **B11**, 222 (1930).

Two conclusions may be drawn from these qualitative considerations: Because the metallic electrons cannot maintain the proper phase with the rotating molecular dipoles, the correct interaction law will yield smaller values than (1); the properties of the metal must enter explicitly. These expectations were verified in a calculation the results of which have been reported by the present authors.[5]

A result perhaps somewhat at variance with these considerations was reported by Prosen, Sachs, and Teller.[6] More recently, Bardeen[7] has made a careful analysis of the problem in which particular attention is directed to the interaction of the electrons within the metal. It also leads to the conclusion that the image force generally yields too strong an attraction. Bardeen's results agree on the whole with those presented in this paper. Although there are several points of contact, the method here used is different and somewhat more in line with the theory of van der Waals forces; we also believe it to be simpler.

II. Preliminary Considerations

We consider the classical interaction energy ΔV between a molecule situated at the origin of coordinates and an elementary portion ω of metal at **D**. By an elementary portion is meant a volume of smaller dimensions than the wavelength of radiation corresponding to the pre-

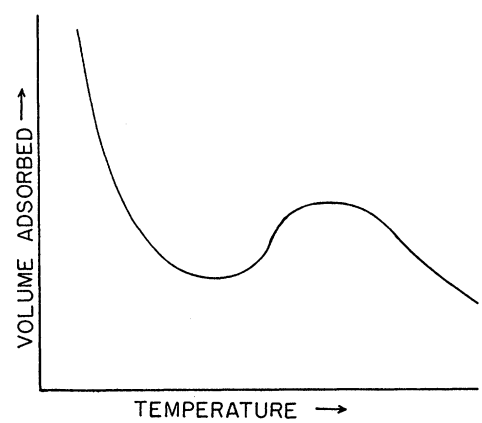

Fig. 1. Typical dependence on temperature of gaseous volume adsorbed.

[5] W. G. Pollard and H. Margenau, Phys. Rev. **57**, 557 (1940).
[6] E. J. R. Prosen, R. G. Sachs, and E. Teller, Phys. Rev. **57**, 1066 (1940).
[7] J. Bardeen, Phys. Rev. **58**, 727 (1940).

dominant resonance frequencies of the molecule, but large enough to possess the bulk properties of the metal. The latter supposition will permit us to compute the total interaction between molecule and metal by summing over the elementary portions; the former requirement is needed to make the formulas for the polarizability, stated [cf. Eq. (5)] and used below, meaningful. With the molecule there is associated, at every instant, a displacement vector $\mathbf{R}^{(1)}$ defined by postulating that the dipole moment be $e\mathbf{R}^{(1)}$. Thus if the molecule is monatomic, $\mathbf{R}^{(1)}=\sum_i \mathbf{r}_i^{(1)}$, the summation extending over the displacements of the individual electrons.

The potential at $\mathbf{D}$ due to the molecular charges at 0 is $\phi(\mathbf{D})=e\mathbf{R}^{(1)}\cdot\mathbf{D}/D^3$. Therefore, if the portion of metal, ω, contains n positive charges at D_i^+ and n negative charges at D_i^- where $i=1, 2, \cdots n$, the mutual potential energy between the molecule and ω will be

$$V=-e^2\sum_i^n [\mathbf{R}^{(1)}\cdot\mathbf{D}_i^+/(D_i^+)^3] + e^2\sum_i^n [\mathbf{R}^{(1)}\cdot\mathbf{D}_i^-/(D_i^-)^3]. \quad (2)$$

If $\mathbf{D}$ is the vector to some fixed point in ω and

$$\mathbf{D}_i^+=\mathbf{D}+\mathbf{r}_i^+, \quad \mathbf{D}_i^-=\mathbf{D}+\mathbf{r}_i^-;$$

V may be expanded provided $|r_i^\pm|\ll D$, yielding the familiar dipole energy

$$V=-e(\mathbf{R}^{(1)}-(\mathbf{R}^{(1)}\cdot\mathbf{D}/D^2)\mathbf{D})\cdot\sum_i e(\mathbf{r}_i^+-\mathbf{r}_i^-)/D^3.$$

The summation appearing here is the dipole moment of ω for which we shall henceforth write $e\mathbf{R}^{(2)}$. When, furthermore, the Z-axis is taken along $\mathbf{D}$, V becomes

$$V=-e^2(X^{(1)}X^{(2)}+Y^{(1)}Y^{(2)}-2Z^{(1)}Z^{(2)})/D^3, \quad (3)$$

$X^{(1)}$, $X^{(2)}$, etc., being the components of the vectors $\mathbf{R}^{(1)}$, $\mathbf{R}^{(2)}$, respectively.

If we assume that the molecule has no permanent dipole moment, the integral of V over the charge distribution of the molecule is zero. The state function of metal+molecule may, for the purpose of calculating van der Waals forces, be taken to be a product of $\psi(1)$ and $\psi(2)$, the former depending only on the state of the molecule, the latter only on the metal. The first-order perturbation is then zero, and the interaction energy is given by

$$\sum_\kappa{}' \frac{|V_{k\kappa}|^2}{E_k-E_\kappa}.$$

Since each state κ depends on the quantum numbers of the molecule (κ_1) and of the metal (κ_2), the energy may be written more explicitly as follows

$$W_\omega=\sum_{\kappa_1\kappa_2}{}' \frac{|(k_1k_2|V|\kappa_1\kappa_2)|^2}{E(k_1)-E(\kappa_1)+E(k_2)-E(\kappa_2)}.$$

In view of (3) this becomes

$$\begin{aligned} W_\omega=-\frac{e^4}{D^6}\sum_{\kappa_1\kappa_2}&[E(\kappa_1)-E(k_1)+E(\kappa_2)-E(k_2)]^{-1} \\ &\times\{|(k_1|X^{(1)}|\kappa_1)(k_2|X^{(2)}|\kappa_2)|^2 \\ &+|(k_1|Y^{(1)}|\kappa_1)(k_2|Y^{(2)}|\kappa_2)|^2 \\ &+4|(k_1|Z^{(1)}|\kappa_1)(k_2|Z^{(2)}|\kappa_2)|^2\}. \quad (4) \end{aligned}$$

The cross terms have disappeared from (4) because in the summation over that part of κ_1 on which the energy of the state $E(\kappa_1)$ does not depend, terms like $X_{k_1\kappa_1}{}^{(1)}$ vanish for a molecule possessing no permanent dipole moment. For dipole molecules, the meaning of W_ω must be modified. See remarks after Eq. (7).

As is customary in calculations of this sort, Eq. (4) will subsequently be transformed by the use of well-known formulas for the "atomic" polarizability. The polarizability of a physical system having instantaneous dipole moment $\mathbf{R}$, due to electrical waves of frequency ν and electric vector along X, is given by

$$\alpha_x(\nu)=2e^2\sum_\kappa \frac{|(k|X|\kappa)|^2[E(\kappa)-E(k)]}{[E(\kappa)-E(k)]^2-(h\nu)^2}. \quad (5)$$

The static polarizability, in accordance with (5), takes the form

$$\alpha_x(0)=2e^2\sum_\kappa [|(k|X|\kappa)|^2/E(\kappa)-E(k)]. \quad (5a)$$

Equation (5) holds for the element of metal as well as the molecule if exact metal wave functions are used in the evaluation of $(k|X|\kappa)$. The fact that these are difficult to calculate need not disturb us here, for the values of α may be taken from experiment or expressed in some other computationally more convenient way.

III. Image Force Formula

In this section it will be shown how Eq. (4) reduces to the expression for the image force. One simply assumes that the energy differences $E(\kappa_1)-E(k_1)$ are much smaller than those for the metal. This implies that the charges in the molecule move more slowly than those in the metal. Under these circumstances the summation over κ_1 appearing in (4) may be carried out and (4) becomes

$$W_\omega = -(e^4/D^6)\cdot\tfrac{1}{3}(k_1|R^{(1)^2}|k_1) \cdot\sum_{\kappa_2}[6|(k_2|X^{(2)}|\kappa_2)|^2/E(\kappa_2)-E(k_2)], \quad (6)$$

provided it is proper to put

$$(k_1|X^{(1)^2}|\kappa_1)=(k_1|Y^{(1)^2}|\kappa_1) =(k_1|Z^{(1)^2}|\kappa_1)=\tfrac{1}{3}(k_1|R^{(1)^2}|\kappa_1) \quad (7)$$

for the ground state k_1. Similar relations are assumed to hold for the metal. Eq. (7) is obvious when the molecule has a spherically symmetrical charge distribution. Otherwise it is necessary to perform, in addition to the summation over κ_1 indicated in (4), an average over all orientations of the molecule in state k_1, and (6) represents this average. Assumption (7) with respect to the metal implies equal polarizabilities in all directions. With the use of (5a),

$$W_\omega = -(e^2/D^6)(k_1|R^{(1)^2}|k_1)\alpha^{(2)}(0).$$

The static polarizability of a metal is its volume divided by 2π, as is known from an elementary argument.[8] Therefore, the interaction energy between the molecule and the entire metal, which is taken to be infinite in both the X and Y directions but extends along Z from D_0 to ∞, will be

$$W=-\frac{e^2}{2\pi}(k_1|R^{(1)^2}|k_1)\int\frac{d\tau}{D^6}=-\frac{e^2(k_1|R^{(1)^2}|k_1)}{12D_0{}^3}.$$

This is Lennard-Jones' formula (1). The present derivation emphasizes its inadequacy for the case of non-polar molecules which have significant energy differences $E(\kappa_1)-E(k_1)$ far greater than the metal, and their neglect falsifies the result completely. On the other hand, if the molecule is rigid and possesses a permanent dipole moment so that its energy differences are those appearing in rotational band lines, the neglect is permissible and (1) should be nearly correct. In physical terms, the electrons in the metal are able to maintain the proper phase with the slowly rotating dipole, but not with the rapidly revolving electrons in a non-polar atom or molecule.

Since $E(k_1)-E(\kappa_1)$ is positive for every κ_1 when k_1 denotes the ground state, it is also clear that the image force law gives too large a result for W.

IV. General Formula

In treating the problem further, restriction will at once be made to molecules having a spherical charge distribution. Equation (4) then reduces to

$$W_\omega = 6S,$$

where

$$S=-\frac{e^4}{D^6}\sum_{\kappa_1\kappa_2}\frac{|(k_1|X^{(1)}|\kappa_1)|^2|(k_2|X^{(2)}|\kappa_2)|^2}{E(\kappa_1)-E(k_1)+E(\kappa_2)-E(k_2)}. \quad (8)$$

After multiplying numerator and denominator of each term in this expression by $[E(\kappa_1)-E(k_1)]-[E(\kappa_2)-E(k_2)]$ there results, on using (5),

$$S=-\frac{e^2}{2D^6}\{\sum_{\kappa_1}\alpha^{(2)}(\nu_{\kappa_1})|(k_1|X^{(1)}|\kappa_1)|^2 +\sum_{\kappa_2}\alpha^{(1)}(\nu_{\kappa_2})|(k_2|X^{(2)}|\kappa_1)|^2=S_1+S_2. \quad (9)$$

Here $\alpha^{(2)}(\nu_{\kappa_1})$ is the polarizability of the metal at the frequency ν_{κ_1} corresponding to the transition of the molecule from the state κ_1 to the ground state k_1; $e|X^{(1)}|$ is the dipole moment connected with that transition. In the second part of (9) the summation is over the polarizabilities of the molecule at the resonance frequencies of the metal, multiplied by the matrix elements of the corresponding transitions.

The first summation occurring in (9) may be evaluated empirically if $\alpha^{(2)}$, obtainable from the optical properties of the metal, is known as a function of the frequency. The matrix elements $|(k_1|X^{(1)}|\kappa_1)|^2$ are simply related to the f values of the molecular transitions. The calculation of S_1 is particularly easy when the visiting molecule is one whose resonance frequencies lie in the ultraviolet and whose dispersive properties are well described by a one-term dispersion formula.

[8] A slab of metal in an electric field E acquires a surface charge of density $\sigma=E/2\pi$. If its thickness is d and its area A its dipole moment is $\sigma Ad=E\tau/2\pi$ where τ denotes its volume.

TABLE I. *Interaction energies, in volts, at a distance 10^{-8} cm from the surface of the metal. Last column for* Na *represents interaction between metal ions and the visiting molecule.*

		W_1	W_2	W	BARDEEN	IMAGE FORCE	W_{ions}
	He	0.01	−0.16	−0.15	−0.12	−0.61	
	Ne	0.01	−0.30	−0.29	−0.24	−1.25	
Cs	A	0.07	−1.25	−1.18	−0.92	−3.54	
	H_2	0.04	−0.62	−0.58	−0.42	−1.40	
	N_2	0.08	−1.33	−1.25	−1.11	−3.95	
	He	0.02	−0.23	−0.21	−0.16	−0.61	−0.013
	Ne	0.03	−0.43	−0.40	−0.32	−1.25	−0.025
Na	A	0.20	−1.80	−1.60	−1.19	−3.54	−0.087
	H_2	0.12	−0.89	−0.77	−0.53	−1.40	−0.038
	N_2	0.24	−1.92	−1.68	−1.42	−3.95	−0.086
	He	0.04	−0.30	−0.26	−0.20	−0.61	
	Ne	0.08	−0.57	−0.49	−0.39	−1.25	
Ag	A	0.47	−2.37	−1.90	−1.42	−3.54	
	H_2	0.28	−1.18	−0.90	−0.62	−1.40	
	N_2	0.55	−2.53	−1.98	−1.78	−3.95	
	He	0.05	−0.31	−0.27	−0.20	−0.61	
	Ne	0.09	−0.59	−0.51	−0.40	−1.25	
Pt	A	0.53	−2.49	−1.96	−1.46	−3.54	
	H_2	0.32	−1.23	−0.92	−0.64	−1.40	
	N_2	0.62	−2.65	−2.03	−1.72	−3.95	
	He	0.06	−0.34	−0.28	−0.21	−0.61	
	Ne	0.11	−0.64	−0.53	−0.42	−1.25	
Cu	A	0.67	−2.69	−2.02	−1.52	−3.54	
	H_2	0.41	−1.34	−0.93	−0.67	−1.40	
	N_2	0.80	−2.88	−2.08	−1.80	−3.95	

Since this is true for most of the simpler molecules, these assumptions will here be made. The summation over κ_1 then reduces to a single term and one obtains

$$S_1 = -\frac{e^2\hbar^2}{4mD^6}\alpha^{(2)}(\nu_1)\frac{f_1}{h\nu_1}, \tag{10}$$

since the oscillator strength of the resonance transition having frequency ν_1 is related to the matrix element by

$$f_1 = \frac{2mh\nu_1}{\hbar^2}|(k_1|X|\kappa_1)|^2.$$

The second summation in (9) is a little more difficult to handle. First, we shall present a simple evaluation which is rather crude but shows the physical meaning and order of magnitude of the term. Since the metallic transitions ν_{κ_2} are generally of smaller frequency than the resonance frequencies of the molecule, the polarizability of the latter, $\alpha^{(1)}(\nu_{\kappa_2})$, may be approximated by its static value $\alpha^{(1)}(0)$, obtainable from the dielectric constant of the gas. This leaves us with the calculation of $\sum_{\kappa_2}|(k_2|X|\kappa_2)|^2$. If, however, we multiply numerator and denominator of each term in this sum by $[E(\kappa_2)-E(k_2)]$ the result may be written, in view of (5a)

$$\frac{1}{2e^2}\Delta E_{\text{Av}}{}^{(2)}\alpha^{(2)}(0),$$

where $\Delta E_{\text{Av}}{}^{(2)}$ is some rather vague mean excitation energy of the electrons in the metal, which one might estimate to be of the order of several volts. As pointed out in the previous section, $\alpha^{(2)}(0)=d\tau/2\pi$. On substituting these results in (9) one has

$$S=\left[-\frac{e^2\hbar^2}{4m}\frac{f_1}{h\nu_1}A^{(2)}(\nu_1)-\frac{1}{8\pi}\alpha^{(1)}(0)\Delta E_{\text{Av}}{}^{(2)}\right]\frac{d\tau}{D^6}, \tag{11}$$

provided $A^{(2)}$ stands for the polarizability per unit volume of the metal so that $\alpha^{(2)}=A^{(2)}d\tau$. By (8) Eq. (11) must be multiplied by 6 to give W_ω and this is to be integrated over $d\tau$ to yield W. Hence

$$\begin{aligned} W &= -\left[\frac{e^2\hbar}{m}A^{(2)}(\nu_1)\frac{f_1}{\nu_1}+\Delta E_{\text{Av}}{}^{(2)}\alpha^{(1)}(0)\right]\Big/8D_0{}^3 \\ &= \quad W_1 \quad + \quad W_2. \end{aligned} \tag{12}$$

A satisfactory estimate of the uncertain $\Delta E_{\text{Av}}{}^{(2)}$ can be obtained from the work of Bardeen.[7] To see the connection between his analysis and the present we return to Eq. (2) which is the same as Bardeen's. This may be written

$$V=\mathbf{R}^{(1)}\cdot\text{grad}V,$$

if by grad$V$ is meant the operation with respect to any one of the $\mathbf{r}_i{}^{(1)}$, the coordinates of the molecular electrons. It is to be noted that grad$V$ depends only on the metal. If now we follow the procedure which led to Eq. (9) we find, in place of $6S_2$, the expression

$$W_2=-\sum_{\kappa_1\kappa_2}\frac{|(k_1|X^{(1)}|\kappa_1)|^2|(k_2|\text{grad}_xV|\kappa_2)|^2+|(k_1|Y|\kappa_1)|^2|(k_2|\text{grad}_yV|\kappa_2)|^2+|(k_1|Z|\kappa_1)|^2|(k_2|\text{grad}_zV|\kappa_2)|^2}{[E(\kappa_1)-E(k_1)]^2-(h\nu_{\kappa_2})^2}\cdot(E(\kappa_1)-E(k_1)),$$

which, for a symmetrical molecule, reduces to

$$-\frac{1}{2e^2}\sum_{\kappa_2}\alpha^{(1)}(\nu_{\kappa_2})\,|(k_2|\text{ grad }V|\kappa_2)|^2,$$

again because of (5). Since all ν_{κ_2} are presumably far from the absorption region of the molecule, $\alpha^{(1)}(\nu_{\kappa_2})$ may be replaced by its static value. Then

$$W_2=-\frac{\alpha^{(1)}(0)}{2e^2}\sum_{\kappa_2}|(k_2|\text{ grad}V|\kappa_2)|^2$$
$$=-\frac{\alpha^{(1)}(0)}{2e^2}(k_2|(\text{grad}V)^2|k_2).$$

Now the matrix element $(k_2|(\text{grad}V)^2|k_2)$ for the ground state of the metal has been evaluated by Bardeen who finds it to be $Ce^4/8r_sD_0^3$ when computed for the entire metal (from $z=D_0$ to $z=\infty$). Here C is a numerical constant approximately equal to 2.5, r_s is the radius of a sphere containing one metal electron. Hence

$$W_2=-Ce^2\alpha^{(1)}/16r_sD_0^3.$$

This is to be identified with the second term in (12). We see, therefore, that the average excitation energy of the metal is given by

$$\Delta E_{\text{Av}}^{(2)}=Ce^2/2r_s. \tag{13}$$

The energy W_2 appears also in Bardeen's work, it is the same as his W_B; but it enters into his final formula in a different and somewhat less conspicuous way.

It is interesting to compare Eq. (12) with the image force formula. For this purpose we may rewrite W_1 in terms of $\langle\mathbf{R}_1^2\rangle_{\text{Av}}$ by using $\hbar f_1/m\nu_1=(4\pi/3)\langle R_1^2\rangle_{\text{Av}}$. This converts Eq. (12) into

$$W=-\frac{\pi e^2\langle R_1^2\rangle_{\text{Av}}}{6D_0^3}A^{(2)}(\nu_1)+W_2. \tag{12'}$$

In order to compare the image potential with this expression, Eq. (1) may be rewritten so as to include the static polarizability $A^{(2)}(0)=1/2\pi$ of the metal. Equation (1) then becomes

$$W=-\frac{\pi e^2\langle R_1^2\rangle_{\text{Av}}}{6D_0^3}A^{(2)}(0). \tag{1'}$$

It is seen that (12′) reduces to the image law (1′) when W_2 is neglected and ν_1 is equated to 0 in W_1. These errors compensate to a considerable extent. While on the image force picture W_1 accounts for the entire interaction, W_2 is the main constituent of Eq. (12′). Indeed $A^{(2)}(\nu_1)$ is negative for the resonance frequencies of the molecule so that W_1 gives rise to a repulsion, as the tables show. Thus all resemblance of our final formula with the image law is lost.

V. Numerical Values

The resonance frequencies of all the molecules for which computations are made in this section are much higher than those of the absorption bands of the metals. For such frequencies the polarizability $A^{(2)}(\nu_1)$ of the metal is given by the simple relation,[9]

$$A^{(2)}(\nu_1)=-n_0e^2/4\pi^2m\nu_1^2,$$

where n_0 is the actual number of free electrons per unit volume of the metal and m is their true mass. The values of f_1, ν_1 and $\alpha^{(1)}(0)$ have been taken from a tabulation published by one of us.[10] In Table I are listed the values of W_1 and W_2 separately for various gases adsorbed on monovalent metals. The values tabulated are the various energies in volts at a distance of 10^{-8} cm from the surface of the metal and so represent the coefficient in volts of $1/D_0^3$ for

Table II. *Interaction energies, in volts, at a distance 10^{-8} cm from the surface of bivalent metals.*

	W_1	W_2	W	Bardeen	Metal
He	0.19	−0.48	−0.29	−0.26	
Ne	0.32	−0.91	−0.59	−0.53	
A	2.00	−3.79	−1.79	−1.82	Be
H_2	1.22	−1.88	−0.66	−0.78	
N_2	2.38	−4.04	−1.66	−2.13	
He	0.08	−0.38	−0.30	−0.23	
Ne	0.15	−0.72	−0.57	−0.46	
A	0.95	−3.02	−2.07	−1.63	Zn, Cd, Hg,
H_2	0.58	−1.50	−0.92	−0.71	rough average
N_2	1.13	−3.23	−2.10	−1.92	
He	0.04	−0.28	−0.24	−0.19	
Ne	0.06	−0.53	−0.47	−0.37	
A	0.39	−2.22	−1.83	−1.36	Mg, Ca, Sr, Ba
H_2	0.24	−1.10	−0.86	−0.60	rough average
N_2	0.46	−2.37	−1.91	−1.61	

[9] Cf. N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Oxford University Press, 1936), p. 115; F. Seitz, *Modern Theory of Solids* (McGraw-Hill, 1940), p. 641.

[10] H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).

each W when D_0 is in angstroms. Table I also shows a comparison of the results here obtained with those of Bardeen and the image force law. The former values were computed from the relation[7]

$$W = -(e^2\langle R_1^2\rangle_{Av}/12D_0^3)(Ce^2/2r_s h\nu_1/1+Ce^2/2r_s h\nu_1)$$

developed by Bardeen, and the latter were obtained from Eq. (1). The agreement with Bardeen's theory appears on the whole satisfactory, although the values obtained from the latter are always lower than ours. Table II contains similar data for divalent metals.

The interaction between the metal ions and the visiting molecule is of course included in the basic formulas (9) and (11). But the approximations made in evaluating $A^{(2)}$ and $\Delta E_{Av}^{(2)}$ ignore this effect. It is therefore of interest to calculate it separately in order to exhibit its order of magnitude. This was done by the methods of reference 4 for the metal Na only. The interaction energy is also proportional to D_0^{-3}; the coefficient, in the same units as the others, is given in the last column of Table I. Clearly, this effect is generally negligible in comparison with that expressed by Eq. (12).

JULY 15, 1941 PHYSICAL REVIEW VOLUME 60

Magnetic Studies of Solid Solutions

II. The Properties of Quenched Copper-Iron Alloys

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(Received April 28, 1941)

The alloys of copper and iron which have been studied show unusual magnetic properties both in the saturation effects at low temperatures and in the apparent change in the magnetic moment of the dissolved iron atoms over the range of temperatures from 14°K to 1300°K. Further research is required on other alloy systems containing transition elements dissolved in the noble metals in order to ascertain whether the phenomena are due to fundamental magnetic properties or due to the state of aggregation of the iron atoms.

In the first paper of this series[1] the authors described a method of measurement which has been used again for the present experiments. The only difference in this case is that the location of the specimen in the magnet has been changed slightly in order to have stable equilibrium and that the furnace of Fig. 2, Part I, has been replaced by a Dewar flask for low temperature measurements. The specimens were in an atmosphere of hydrogen for all experiments except those below 60°K for which a mixture of hydrogen and helium was used.

Some preliminary results presented in Part I on alloys of copper with small percentages of iron showed that the magnetic properties depended in a complicated way on the heat treatment of the specimens. In an effort to narrow the range of investigation, the present experiments have been confined to that state of the alloys in which all the iron is believed to be in solid solution. This state surely exists in the high temperature measurements above the solubility limits and it is assumed to exist for all the present experiments at room temperature and below because each of the specimens was quenched in water from above the solubility limits.

The alloys for this investigation were made by dissolving iron in molten electrolytic copper in an atmosphere of hydrogen and then chill casting in vacuum. The castings were annealed for 5 days at 1000°C and then quenched after which they were swaged to the desired size. Samples for measurement were cut from this stock and prepared by annealing the low iron alloys at 950°C and the

[1] F. Bitter and A. Kaufmann, Phys. Rev. 56, 1044 (1939).