FORCES AND ADSORPTION AT SOLID SURFACES

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ABSTRACT

Essentially all interactions between atoms, molecules and ions spring from the electrical charges borne by the nuclei and electrons of which they are constituted. Two broad classes of interaction are distinguished by the terms "chemical" and "physical," the former referring to those cases wherein some of the electrons of the two participants have become shared, with the consequent formation of a chemical bond. Such chemical forces have the property of saturation, are of very short range, and are usually associated with the comparatively large binding energies of a few electron volts. Some of the more important types of physical interactions, listed more or less in order of decreasing energy, are: ion-ion, ion-dipole, dipole-dipole, ion-induced dipole, induced dipole-induced dipole, etc. Those not involving ions are often grouped together under the term "van der Waals forces," and generally have energies of only a fraction of an electron volt. The (long-range) ion-ion interactions ("ionic bonds") are mainly responsible for the stability of ionic crystals, and thus may have energies comparable with those of chemical bonds.

An adsorbed molecule interacts very nearly additively with all the constituent atoms and ions of the adsorbent surface, and with other adsorbed molecules as well. The collective effect may be described through the "energy of adsorption," which will generally be a function of the amount adsorbed. In physical adsorption, multilayer films and capillary condensation may occur at gas pressures approaching saturation.

The small size and high dipole moment of the water molecule make it strongly adsorbed on ionic substrates. The lamilar structure of the clay minerals furnishes enormous surface areas for adsorption. Investigation of these interactions at the molecular level provides a fundamental basis for a more complete understanding of clay-water systems.

INTRODUCTION

The principles governing the interactions of individual atoms and molecules have been understood in all essential detail since shortly after the discovery of quantum mechanics nearly thirty years ago. It is the purpose of the present discussion to summarize those results pertinent to an understanding of the adsorption of condensable gases at solid surfaces.

A complete knowledge of the interaction of two molecules is generally assumed as the point of departure from which statistical mechanical theories proceed to describe the macroscopic properties of those molecular assemblages of special interest. Fortunately, a qualitative understanding of many aspects of adsorption can be gained without a detailed solution of the many-particle statistical mechanical problem. While the omission of such elaboration permits a far less sophisticated approach, it has the lamentable consequence of limiting the discussion to topics now rather remote from the frontiers of current research; indeed, most of the subjects considered here

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have long since found their way into one or another standard treatise (Brunauer, 1943).

There will be little space devoted to any special properties of clays other than the fact that they provide large surface areas on which adsorption is energetically favorable. Thus, although clays play no very unique role in adsorption, adsorption — more particularly, the adsorption of water — plays a dominant role in determining the physical properties of clay-water systems.

TYPES OF INTERACTION

At the outset we distinguish two principal types of interatomic forces. On the one hand are the chemical or valence forces, characterized by the property of saturation (in that each atom can participate in only a limited and small number of chemical bonds), by relatively high bond energies (of the order of a few electron votes *), and often by the requirement of an energy of activation for bond formation. Only in exceptional cases are these valence forces not completely satisfied in normal molecules and ions. However, among these exceptions are two instances of importance in adsorption: first, by virtue of their unsymmetrical environment, the atoms in the surface of a solid may have residual bond-forming ability, leading to *chemisorption;* second, the water molecule exhibits a propensity for forming "hydrogen bonds."

In contrast, the physical forces are generally characterized by their approximate additivity and lack of saturation (except as dictated by geometrical limitations on the permissible number of "nearest neighbors"), by comparatively low interaction energies (perhaps a fraction of an e.v.), and by the absence of an activation energy. We shall be mainly concerned with this second type of interaction, which gives rise to *physical adsorption.*

The constitution of atoms of electrically charged nuclei and electrons might suggest that a complete description of atomic interaction should be contained in Coulomb's Law. The finite size of atoms indicates that this is not the case. The lowest electrostatic energy evidently would obtain when the positions of positive and negative charge coincide. That actual atoms do not so collapse is explained in quantum mechanics by the fact that confinement of a particle (*e.g.,* an orbital electron) to a smaller and smaller volume about the nucleus causes its kinetic energy to increase and ultimately over-compensate the consequent decrease in electrostatic energy. Again, any attempt to superimpose two atoms encounters at sufficiently close distances a strong repulsion, which arises in part from another strictly quantum mechanical result ("statistical repulsion") that the electrons cannot occupy a region of space already occupied by other electrons without going to higher energy states. For our purposes it will suffice to recognize that atoms, molecules and ions have characteristic sizes, and that energies of very considerable magnitude, not usually available in adsorption proc-

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* One electron volt (e.v.) is equivalent to $1.6 \cdot 10^{-12}$ erg/particle, or 23 kcal/mole.

esses, are required to achieve densities much above that of the normal condensed state.

RIGID CHARGE DISTRIBUTIONS

Although inadequate for mobile charges, classical electrostatic theory gives an exact description of the interactions of rigid charge distributions. Owing to differences in the electron-attracting ability, or "electronegativity," of various types of atoms, the charge distribution in a molecule will generally not be symmetric. Insofar as the asymmetry may be described in terms of fixed charges q_i rigidly attached to the molecular framework at positions r_i (Joos, 1934) the classical electrostatic potential $V(\mathbf{R})$ at vectorial distance $\mathbf{R}$ (assumed large compared with the molecular extension) from the molecule is given by

$$V(\mathbf{R}) = q/R + \mu \mathbf{R}_1/R^2 + \ldots, \tag{1}$$

where

$$q = \Sigma q_i \tag{2}$$

is the net (monopole) charge on the molecule as a whole, $\mathbf{R}_1$ is a unit vector along $\mathbf{R}$, and

$$\mu = \Sigma q_i \mathbf{r}_i \tag{3}$$

is the "dipole moment" of the distribution. Higher multipole terms, omitted from Eq. (1), will not be considered here, although they may occasionally be important.

If the molecule is ionized, its potential at large distances will be governed by the monopole term. The interaction of such monopoles is, of course, the main source of the high binding energies characteristic of ionic crystals. However, we shall rather arbitrarily limit this discussion to the interaction of two molecules of which at least one is neutral. This excludes the important process of ion exchange, which is presumed to lie outside the present assignment.

For a neutral molecule, obviously the second term of the expansion (1) will dominate provided μ does not vanish. By grouping together terms of like sign in the definition (3),

$$\mu = \Sigma q_i \mathbf{r}_i^- + \Sigma q_j \mathbf{r}_j^+$$
$$= (\Sigma q_j)(\{\mathbf{r}^+\} - \{\mathbf{r}^-\}) = q\mathbf{s}, \tag{4}$$

we see that the dipole moment is expressible as the product of the total charge q of one sign with the distance **s** of separation between the mean † positions of the positive and negative charges. The displacement of one electronic charge through a distance of one Angstrom unit would yield a dipole moment of magnitude $4.8 \cdot 10^{-18}$ e.s.u. Values of μ for selected molecules will be given later (column 2, Table I).

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† Average values will be indicated by braces { }; the distribution over which the average is taken will be made clear from the context.

The interaction energy of a point dipole μ, in fixed orientation, with a monopole of charge q is given by

$$\epsilon_{q\mu} = q\mu R_1/R^2. \tag{5}$$

Ion-dipole forces are largely responsible for the affinity of polar solvents for ionic solutes, as evidenced by solubility, heat of solution, degree of solvation, etc. Ion-dipole interactions also often contribute importantly to the interactions of molecules with surfaces, although probably seldom under circumstances where the approximation of the dipole as a point is valid.

The interaction energy $\epsilon_{E\mu}$ of a dipole μ with an external field $\mathbf{E}$ is

$$\epsilon_{E\mu} = -\mu E \tag{6}$$

above the value corresponding to orientation perpendicular to the field. At (absolute) temperature T a given orientation will be weighted by the Boltzmann factor, $\exp(\mu E/kT)$. For small values of the exponent, this factor may be expanded in the usual power series. Retaining terms to first order in $\mu E/kT$, one thus finds for the mean interaction energy, averaged over all orientations of μ,

$$\epsilon = -\{\mu E(1 + \mu E/kT)\} = -\mu^2 E^2/3kT. \tag{7}$$

If the field $\mathbf{E}$ arises from a second dipole μ', then by definition

$$\mathbf{E}(\mu', \mathbf{R}) = -\mathrm{grad}(\mu' R_1/R^2) = [\mu' - 3(\mu' R_1)R_1]/R^3. \tag{8}$$

Repeating the above calculation with this expression for $\mathbf{E}$, but now averaging over all orientations of both dipoles (at fixed $\mathbf{R}$) gives for the mean dipole-dipole interaction energy

$$\epsilon_{\mu\mu} = -2\mu^2 \mu'^2/3kTR^6. \tag{9}$$

It is important to notice that if the two dipoles were rotating freely, *i.e.*, without the Boltzmann factor favoring those orientations of least energy, there would be no net interaction energy. In other words, the energy of attraction predicted by Eq. (9) is due entirely to *correlations* in the orientations of the two dipoles. These correlations are opposed by thermal agitation, and vanish in the limit of infinite temperature.

MOBILE CHARGE DISTRIBUTIONS

So far we have considered only rigid charges, which were required to maintain their distribution relative to the molecular skeleton. We now recognize that the charge distribution in a molecule is not entirely rigid, but can be distorted by the application of an external field.

In the simplest case where the molecule has sufficiently high symmetry, the electrical distortion, as measured by the induced dipole moment $a\mathbf{E}$, is proportional to the applied field $\mathbf{E}$. The proportionality constant a is known as the "polarizability." In the general case the induced dipole will not be parallel to $\mathbf{E}$, and a will have a more complicated interpretation. Neverthe-

less, one can define an orientationally-averaged polarizability, which is the quantity generally measured. With this simplification, the energy of interaction of the induced dipole with the applied field is

$$\epsilon_{Ea} = -a E^2/2,$$ (10)

as may be seen from the fact that the elastic distortion of the harmonically-bound charge distribution requires an energy just half that of the interaction of the resulting dipole $a\mathbf{E}$ with the field $\mathbf{E}$ (cf. Eq. (6)).

For the interaction energy between an ion having field $\mathbf{E}_i = q\mathbf{R}_i/R^2$ and a molecule of polarizability a, Eq. (10) gives

$$\epsilon = -a q^2/2R^4.$$ (11)

Employing Eq. (8), the dipole-polarizability interaction, again averaged over all orientations of the permanent dipole moment, is

$$\epsilon_{\mu a} = -a\mu^2/R^6.$$ (12)

As in the case of dipole-dipole interaction, this energy is intrinsically negative, indicating attraction, and results from correlations of the electronic motions within the polarizable molecule with the changing orientation of the inducing dipole.

This point of view suggests that even nonpolar molecules may interact through correlations of their respective electronic motions. That this is indeed the case was first shown by London (1930). We may arrive at the essential form of this polarizability-polarizability (or "dispersion") energy ϵ_{aa} by the following heuristic argument (Rice and Teller, 1949).

In a crude sense, an atom may be regarded as having an instantaneous dipole moment, corresponding to the possibility of finding the electrons instantaneously in a nonsymmetrical configuration. This dipole, of course, has average value zero, fluctuating in both magnitude and direction as a result of the electronic kinetic energy, a quantity measured by the energy $h\nu$ corresponding to the natural response frequency ν of the electrons. The interaction of two such instantaneous dipoles is thus quite similar to that of two permanent dipoles discussed in connection with Eq. (9). Interpreting Eq. (7) in the light of Eq. (10), the effective (orientational) polarizability a_0 of a permanent dipole μ, suffering a thermal agitation measured by kT, is, apart from numerical factors,

$$a_0 \sim \mu^2/kT.$$ (13)

By analogy, we might thus expect to find μ^2 in Eq. (9) replaced by $ah\nu$, and the role of kT assumed by the mean value $h(\nu+\nu')/2$, to give for the dispersion energy of two dissimilar molecules,

$$\epsilon_{aa} \sim -2(ah\nu)(a'h\nu')/h(\nu+\nu')R^6.$$ (14)

The rigorous quantum mechanical treatment gives precisely this result multiplied by $\frac{3}{4}$.

Although in polar molecules the dispersion forces may be dominated by

the effects of permanent dipole moments, in nonpolar molecules they are manifested in gas imperfections, condensation and adsorption. They are not negligible even in ionic crystals, being a decisive factor in determining whether a given alkali halide normally crystallizes in the face-centered or body-centered lattice.

The fact that all three energies $\epsilon_{\mu\mu}$, $\epsilon_{\mu a}$ and ϵ_{aa} depend in the same way upon R allows a comparison of the coefficients of R^{-6}. Such a comparison, for interactions between identical molecules at $T = 293°$ K, is shown in Table I, recalculated from London (1937). Here energies are expressed

Table I. — The Interaction Energies of Some Neutral Molecules

	μ	α	$h\nu$	$R^6\epsilon_{\mu\mu}$	$2R^6\epsilon_{\mu a}$	$R^6\epsilon_{aa}$
CO	0.12	1.99	14.3	0.0021	0.036	42
HI	0.38	5.4	12	0.22	1.05	239
HBr	0.78	3.58	13.3	3.9	2.53	110
HCl	1.03	2.63	13.7	11.6	3.4	66
NH₃	1.5	2.21	16	53	6.3	58
H₂O	1.84	1.48	18	119	6.3	29

in e.v., distances in Angstrom units, and the dipole moment in Debye (10^{-18} e.s.u.).

The total interaction energy is, of course, given by the sum

$$\epsilon = \epsilon_{\mu\mu} + 2\epsilon_{\mu a} + \epsilon_{aa} . \tag{15}$$

As London has shown, this theory gives beautiful agreement with measured values of the second virial coefficient and the heat of vaporization.

SURFACE FORCES

The interaction of an adsorbed molecule with the adsorbent is nothing more than the totality of interactions with the individual atoms, molecules or ions composing the adsorbent. For example, the dispersion energy, being very nearly additive, may be calculated by summing (or, approximately, integrating) Eq. (14) over the three dimensions of the adsorbent. This evidently results in an inverse cube dependence of the attraction energy upon R. In computing the attractive energy near the surface of an ionic crystal, one must also calculate the net field **E** as a function of position and then proceed to use one or both of Eqs. (6) and (10). In comparison with the energy of a pair of molecules, the adsorption potential is not only far greater at the distance of closest approach, but also falls off more slowly with increasing distance. These two qualities lead to measurable adsorption at pressures where there is almost immeasurable deviation of the gas from ideality.

For physical forces one expects adsorption energies of magnitudes comparable with energies of liquefaction, and such is the case. Again the

theory outlined above finds excellent agreement with experiment. For example, recent work by Fisher (1954) in this laboratory has given the comparison between theoretical and experimental energies of adsorption of krypton, methane, and nitrogen on sodium bromide shown in Table II.

TABLE II. — ENERGIES OF ADSORPTION (IN e.v.) ON SODIUM BROMIDE

	Theory	Experiment[1]
Kr	0.134	0.137
CH₄	0.126	0.130
N₂	0.048	0.096

[1] Evaluated from the experimental adsorption isotherms.

The large deviation for nitrogen undoubtedly results from treating the polarizability as a scalar: with this approximation one predicts an adsorption energy smaller than that which obtains in the preferred orientation.

As a matter of current interest it might be mentioned that, under appropriate conditions, the forces between adsorbed molecules acting parallel to the adsorbent surface may give rise to "two-dimensional condensations." Again these "lateral interactions" have their origins in the effects discussed above, and may be calculated as before.

THE ADSORPTION ISOTHERM

From a thermodynamic standpoint, the condition for equilibrium in a system (here, the adsorbent, the adsorbed phase and the vapor) at constant volume, temperature and number of molecules is that the Helmholtz free energy, F, be a minimum. This quantity is the difference between the energy E of the system and the product of the absolute temperature T with the entropy S of the system:

$$F = E - TS. \tag{16}$$

Because the molecules are attracted to the surface, it is clear that the energy of an adsorbed molecule is lower than that of a molecule in the vapor phase. However, an adsorbed molecule is confined to the surface layer and has its freedom of motion seriously restricted in comparison with that in the vapor. This greater regimentation in the adsorbed phase is reflected in a smaller entropy, so that both E and S decrease as the number of molecules in the surface increases. The energy of adsorption generally declines with increasing amount adsorbed, whereas in the vapor phase there is an increasing volume per molecule causing the entropy decrement on adsorption to increase. Adsorption therefore progresses until the energy of adsorption can no longer compensate for the entropy of adsorption. If at this point the density of the vapor is increased, say by decreasing the volume, more adsorption occurs until once again equilibrium is attained.

Broadly speaking, there are three ranges of adsorption, according to

whether the extent of adsorption is: (a) below a monomolecular layer; (b) multilayer on a free surface; or (c) multilayer on a restricted surface, *e.g.,* in capillaries, cracks or spaces between particles.

To illustrate, we may trace the course of a typical adsorption isotherm, *i.e.,* a plot of the amount adsorbed as a function of the equilibrium adsorption pressure, on a material having capillaries of sufficiently large diameter to exhibit all three ranges. Since there is usually some degree of nonuniformity of the surface, those sites having a large adsorption energy will become occupied first. Where the energy of adsorption is large relative to the energy of liquefaction of the gas one finds an initial rapid rise in the amount adsorbed with increasing pressure.

In the neighborhood of a monomolecular layer, the energy of adsorption usually drops rather abruptly, so that the amount adsorbed thereafter increases rather slowly with increasing pressure. In this region the adsorbed phase presumably progresses from a monomolecular layer to a liquid-like multimolecular layer having more or less uniform thickness. As the density of the vapor nears its saturation value, the volume per vapor molecule becomes smaller, and once again the amount adsorbed increases rapidly with increasing pressure.

In the absence of restrictions on the thickness, the adsorbed layer should go over continuously into a liquid on reaching the normal saturation pressure of the vapor. However, it may happen that the adsorbed layer growing out from one surface meets and coalesces with another growing toward it from an opposing surface. Such capillary condensation has two consequences which are clearly visible in the isotherm. First, the surface area available to further adsorption is markedly decreased; and second, on lowering the pressure the isotherm exhibits a hysteresis owing to the fact that the coalescence is intrinsically irreversible.

ADSORPTION AS A TOOL

Investigations of the last four decades, starting essentially with Langmuir's (1918) definititive study, have yielded fairly adequate theories for each of the three ranges of adsorption discussed in the last section. Rather than attempt here a summary of this extensive development, we shall mention only two features which provide extremely useful information concerning the nature of the adsorbent from a study of the adsorption isotherms.

The foremost problem in investigations with surfaces is the determination of extent of the surface. One of the easiest and most reliable ways of determining the surface area is the method of Brunauer, Emmett and Teller (1938). Their theory furnishes a way of plotting adsorption data which yields a straight line, at least in the vicinity of a monolayer. The two parameters of the straight line then provide a measure of the energy of adsorption into the first layer and of the number of molecules of the adsorbate constituting a monolayer. The surface area can then be calculated

as the product of this latter quantity with the molecular cross section. If the sample is in finely divided form, the surface area (in the absence of capillaries) permits an estimate of the mean particle size. In this way Emmett and coworkers have determined the surface areas of hundreds of materials, among them clays and soil colloids.

A study of the hysteresis loop in the case of capillary condensation has yielded a great deal of information concerning the internal pore structure of adsorbents, particularly the distribution of pore sizes. This has turned out to be most significant in understanding heterogeneous catalysis and the influence of catalyst poisons.

In the field of ceramics, the properties of clay-water systems are certainly intimately connected with surface forces and structures of the clay. It seems evident that adsorption not only plays a dominant role in determining these properties, but also presents unexploited possibilities for their interpretation in fundamental terms.

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