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Physical Adsorption of Gases

PHYSICAL ADSORPTION OF GASES

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PREFACE

STRINGENT limitations have to be imposed on the scope of a book covering, in a single volume, the literature on physical adsorption since 1930. The present treatment deals only with the adsorption process proper, excluding additional complications such as the capillary phenomena peculiar to porous adsorbents. Furthermore, no attempt has been made to catalogue the myriad gas-solid systems whose properties are reported in the literature. Rather, individual systems have been mentioned only where they illustrate general principles. Only in this way has it been possible to give a coherent account of the subject, supported by an adequate but not irritatingly profuse number of references. Happily, the formidable task of classifying the detailed information on gas-solid systems in the literature has been ably discharged by Deitz in the two editions of *Bibliography of Solid Adsorbents*, leaving writers of books free to devote their attention to the general characteristics of the physical adsorption process.

We are greatly indebted to Professor F. C. Tompkins, F.R.S., who suggested the book, and whose counsel and encouragement have been invaluable. Thanks are also due to Professor R. A. Beebe and Dr. J. A. Morrison for reviewing parts of the chapter on calorimetry, to Professor R. L. McIntosh for reviewing the section on dielectric properties and to Dr. G. J. Young for advice on heats of immersion. One of us (D. M. Y.) wishes to thank his colleague Dr. D. N. Glew for many helpful discussions during the preparation of the manuscript.

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CONTENTS

	Page
PREFACE	v
1. INTRODUCTION	1
General	1
Physical and chemical adsorption	1
The data of adsorption	3
2. PHYSICAL ADSORPTION FORCES	6
Introduction	6
Dispersion forces	7
Dispersion forces between pairs of molecules	7
Dispersion forces between adsorbed molecules and solid surfaces	11
Repulsive forces	17
Repulsive forces between pairs of molecules	17
Combined dispersion and repulsive forces between pairs of molecules	19
Repulsive forces between adsorbed molecules and solid surfaces	23
Interaction of non-polar molecules with non-ionic solids	24
Interaction of non-polar gases with graphite	28
Interaction of non-polar gases with metals	33
Interaction of non-polar gases with semiconductors	34
Charge-transfer no-bond interaction	35
Interaction of non-polar molecules with ionic crystals	37
Interaction of polar molecules with solid surfaces	45
Interaction of polar molecules with conductors	46
Interaction of polar molecules with ionic crystals	46
Interaction of quadrupoles with ionic solids	49
Interaction between adsorbed molecules	51
Interaction between atoms adsorbed on graphite	51
Interaction between argon atoms adsorbed on ionic crystals	55
3. THERMODYNAMICS OF PHYSICAL ADSORPTION	64
Introduction	64
Thermodynamic fundamentals	66
Basic relationships	66
Heats of adsorption	70

CONTENTS

	Page
Thermodynamic relationships for simple models	75
Localized Langmuir monolayer	76
Non-localized van der Waals monolayer	78
BET multilayer	79
Experimental studies of thermodynamic properties of adsorbed layers	82
Thermodynamic functions from isotherms	82
Thermodynamic functions from heats of adsorption	91
Heat capacities of adsorbed layers	96
Phase changes in adsorbed layers	98
4. MONOLAYER ADSORPTION ON UNIFORM SURFACES	104
Adsorption without lateral interactions	104
Henry's Law	104
Ideally localized monolayers: Langmuir's isotherm	106
Analogues of Langmuir's isotherm	109
Mobile monolayers: Volmer's isotherm	110
The localized-mobile transition	113
Adsorption with lateral interactions	113
Regular localized monolayers	113
Mobile monolayers with interaction	116
Two-dimensional condensation	117
Localized monolayers with interaction: critical conditions	118
Mobile monolayers with interaction: critical conditions	119
Experimentally observed phase changes	120
Analogy between adsorbed films on solids and insoluble films on liquids	127
Stepwise isotherms	128
5. MULTILAYER ADSORPTION ON UNIFORM SURFACES	137
Introduction	137
Earlier theories	137
The potential theory	137
The polarization theory	146
The BET equation	147
Introduction	147
Kinetic derivation	148
Statistical derivation	152
Application of the simple BET equation	152
Modifications of the BET isotherm	156
The Hüttig isotherm	157
Criticism of the BET theory	159
The factor $a_1 b_1 / a_2 b_1$	163

CONTENTS

	Page
Refined treatments	164
The Wheeler-Ono approach	164
Refinement of the BET model	166
The Frenkel-Halsey-Hill slab theory	167
Barrer and Robins' theory	170
Stepwise multilayer isotherms	171
6. ESTIMATION OF SURFACE AREAS BY GAS ADSORPTION	182
Introduction	182
Methods for evaluating the monolayer capacity	183
The Langmuir isotherm	183
The Point B method	185
The BET method	190
Modifications of the BET technique	194
The measurement of very low surface areas	197
Relationship between the BET and Point B methods	198
The BET equation for adsorption restricted to n -layers	199
Modifications of the BET equation	202
The Hüttig equation	204
Evaluation of v_m from rate measurements	206
The method of Gregg	208
Other methods for evaluating v_m	210
Methods leading directly to Σ , without any explicit assumption as to the value of σ_m	212
Evaluation of porous adsorbents by the method of Kistler <i>et al.</i> and Harvey	212
The Harkins-Jura relative method	213
Relationship between the HJ and BET equations	214
Methods based on the heat of wetting: the Harkins-Jura absolute method	219
The method of Fu and Bartell for porous solids	221
The method of Steele and Halsey	223
The molecular area	226
The selection of σ_m values	226
Localized and oriented films	230
Molecular sieve effects	230
Comparison of gas adsorption surface areas with those determined by other methods	231
Standard BET areas defined	231
Adsorption from solution	231
Permeability methods	233
Geometrical areas	234
Particle size analysis	235
Miscellaneous methods	238

CONTENTS

	Page
7. ADSORPTION ON NON-UNIFORM SURFACES	247
Introduction	247
Theoretical treatments of monomolecular adsorption	248
Localized adsorption	248
Mobile adsorption	258
Experimental determinations of the distribution function	261
Calorimetric determination	261
Distributions derived from experimental isotherms	265
Theoretical treatments of multilayer adsorption	267
Extension of the BET analogous equations	267
Extension of the slab theory	268
Extension of the potential theory	273
8. THE MEASUREMENT OF ADSORPTION ISOTHERMS	277
Outgassing	277
Volumetric methods	279
General	279
Intermediate pressures	283
Thermal transpiration	283
High pressures (subatmospheric)	284
Condensable vapours	289
The adsorbent cell	291
High pressures (superatmospheric)	293
Gravimetric methods	293
Helical springs: the McBain-Bakr sorption balance	293
Direct weighing on an analytical balance	296
Special balances	297
9. ADSORPTION CALORIMETRY	306
Precision adiabatic calorimeters	306
Simple calorimeters	311
Ice calorimeters	315
Microcalorimeters	317
Heat of immersion calorimeters	318
10. PROPERTIES OF THE ADSORBED LAYER	326
Electric and magnetic properties of adsorbed layers	326
Dielectric properties	326
Conductivity of adsorption systems	337
Surface potentials of adsorbed films	343
Magnetic properties of adsorbed films	348
Magnetic resonance in adsorbed films	351
Infra-red spectroscopy of adsorbed layers	354

CONTENTS

11. THE ADSORPTION OF GAS MIXTURES	<i>Page</i> 365
Introduction	365
Experimental methods	366
General	366
The dynamic method	367
The constant volume method	368
Adsorption from saturated vapours	371
Theoretical treatments	371
General	371
The Langmuir isotherm for mixed gases	373
Mixed mobile monolayers	380
Mixed monolayers on a non-uniform surface	381
The BET theory for mixed gases	384
Other multilayer theories	389
Thermodynamics of mixed adsorption	391
Experimental results	396
Effect of order of admission	396
Selective adsorption from binary mixtures	397
The adsorption relative volatility (α)	401
AUTHOR INDEX	407
SUBJECT INDEX	420

INTRODUCTION

GENERAL

When a gas* is allowed to come to equilibrium with a solid or liquid surface, the concentration of gas molecules is always found to be greater in the immediate vicinity of the surface than in the free gas phase, regardless of the nature of the gas or surface. The process by which this surface excess is formed is termed *adsorption*. In any solid or liquid, the atoms at the surface are subject to unbalanced forces of attraction normal to the surface plane; the balance of forces is partially restored by the adsorption of gas molecules.

Adsorption is to be distinguished from *absorption*, which involves bulk penetration of the gas into the structure of the solid or liquid by some process of diffusion. Since absorption is governed by the laws of diffusion, it can usually be differentiated from adsorption¹. The term *sorption* is applied to cases where both the above processes may be occurring simultaneously.

Adsorption of a gas on a solid is a spontaneous process and is therefore accompanied by a decrease in the free energy of the system. Since the process involves loss of degrees of freedom of the gas, in passing from the free gas to the adsorbed film, there is also a decrease in entropy. It follows from the equation

$$\Delta F = \Delta H - T\Delta S \quad (1)$$

that the adsorption process must always be exothermic. This is true regardless of the nature of the forces involved.

PHYSICAL AND CHEMICAL ADSORPTION

Adsorption processes may be classified as physical or chemical, depending on the nature of the forces involved. *Physical adsorption*, also termed *van der Waals adsorption*, is caused by molecular interaction forces; the formation of a physically adsorbed layer may be likened to the condensation of a vapour to form a liquid. Not only is the heat of physical adsorption of the same order of magnitude as that of

* The term 'gas' will serve to denote gas or vapour. When it is necessary to distinguish between gases and vapours, the terms 'permanent gas' and 'condensable vapour' will be used.

INTRODUCTION

liquefaction, but physically adsorbed layers, particularly those many molecular diameters thick, behave in many respects like two-dimensional liquids. On the other hand, chemical adsorption, usually abbreviated to *chemisorption*, involves transfer of electrons between the solid (or *adsorbent*) and the gas (or *adsorbate*). The process essentially involves the formation of a chemical compound between the adsorbate and the outermost layer of adsorbent atoms.

The distinction between physical adsorption and chemisorption is usually clear cut, but where there is doubt a decision can be made on the basis of one or more of the following criteria:

(a) The heat of physical adsorption is of the same order of magnitude as the heat of liquefaction of the adsorbate and is rarely more than twice or three times as large, whereas the heat of chemisorption is of the same order as that of the corresponding bulk chemical reaction. In some cases, however, exceptionally low heats of chemisorption are found. In making such comparisons it should be noted that in both types of adsorption, because of surface heterogeneity and lateral interaction effects, the heat of adsorption may vary considerably with surface coverage. This effect is particularly marked in chemisorption where the lateral interaction forces, being invariably repulsive, reinforce the effects of heterogeneity.

(b) Physical adsorption, like condensation, is a general phenomenon and will occur with any gas-solid system provided only that the conditions of temperature and pressure are suitable. On the other hand, chemisorption will take place only if the gas is capable of forming a chemical bond with the surface atoms.

(c) A physically adsorbed layer may be removed by reducing the pressure, at the temperature at which adsorption took place, although the process may be slow on account of diffusion effects. The removal of a chemisorbed layer, however, often requires much more rugged conditions, especially on metal surfaces where very high temperatures or positive ion bombardment are needed. An exceptional case is the system oxygen on charcoal, in which the chemisorbed layer is so strongly held that high temperature desorption yields not oxygen but a mixture of carbon monoxide and dioxide.

(d) Under suitable conditions of temperature and pressure, physically adsorbed layers several molecular diameters in thickness are frequently found. In contrast, chemisorption is complete once a monomolecular layer is built up, although physical adsorption may occur on top of the chemisorbed monolayer.

(e) Since physical adsorption is related to the process of liquefaction, it only occurs to an appreciable extent at pressures and temperatures close to those required for liquefaction. Thus if p is the

THE DATA OF ADSORPTION

equilibrium pressure of the adsorbed film and p_0 is the vapour pressure of the bulk liquid at the temperature of the experiment, it is generally found that below $p/p_0 = 0.01$ no significant adsorption takes place. There are some exceptions, notably with adsorbents having very fine pores. On the other hand, chemisorption often proceeds at much lower pressures and much higher temperatures.

(f) Physical adsorption and chemisorption may sometimes be distinguished by their different rates of approach to equilibrium. Physical adsorption *per se* is instantaneous but, with highly porous or finely powdered adsorbents, diffusion of the gas into the adsorbent mass is often slow, particularly at low pressures. Chemisorption may be instantaneous but there are many systems where chemisorption involves an activation energy. In both physical and chemical adsorption, precise measurements may be hampered by the establishment of a pseudo-equilibrium. Thus the outer strata of adsorbent are more heavily covered with adsorbate than the centre of the solid mass; subsequent redistribution of the adsorbed film to give uniform coverage at all points in the solid mass is sometimes an extremely slow process. Clearly, the use of a rate criterion to distinguish physical from chemical adsorption is fraught with complications.

THE DATA OF ADSORPTION

Experimental measurements of the amount adsorbed, v , as a function of pressure and temperature may conveniently be plotted in the form of adsorption isotherms

$$v = f(p)_T \quad (2)$$

Isotherms are essentially plots of the free energy change as a function of amount adsorbed. Their shape can also yield qualitative information about the adsorption process and a semi-quantitative measure of the fraction of the surface covered by adsorbate (and hence, with assumptions, the surface area of the adsorbent). For these reasons and because they can be measured directly, isotherms are the most commonly used p - v - T plot in adsorption studies.

Although adsorption isotherms with shapes ranging from the monotonous to the fantastic have been reported in the literature, the classification introduced by Brunauer *et al.*², for systems at temperatures below the critical temperature of the gas, is nonetheless valuable. Their five basic isotherm shapes are shown in Figure 1.1. Isotherms of Type I are associated with systems where adsorption does not proceed beyond a monomolecular layer. The remainder all involve the multilayer formation. Types IV and V are characteristic of

multilayer adsorption on highly porous adsorbents, the flattening of the isotherms at the highest pressures being attributed to capillary phenomena. Since capillary effects lie outside the scope of this book, reference will only be made to isotherms of Types I, II and III.

Further information can be secured from a study of adsorption isosteres

$$p = f(T)_v \quad (3)$$

These cannot be measured directly because it is impractical to hold v constant. Instead, values of p and T corresponding to fixed values of v are interpolated from a family of adsorption isotherms. Provided

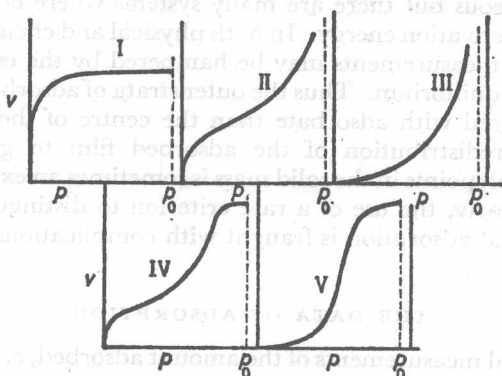


Figure 1.1. The five types of physical adsorption isotherm. p_0 is the saturation vapour pressure. (From Brunauer, *The Adsorption of Gases and Vapours* (1945); by courtesy of the Clarendon Press and Princeton University Press.)

the heat of adsorption does not vary significantly over the temperature range studied, plotting the isosteres in the familiar form $\log p$ vs. $1/T$ will yield a family of straight lines, each corresponding to a fixed value of the amount adsorbed. The linearity of the isosteres, incidentally, provides a useful check on the internal consistency of the isotherms. The heats of adsorption at each amount adsorbed may be calculated from the slopes of the isosteres, using the Clausius-Clapeyron equation in the form

$$\frac{d \ln p}{d(1/T)} = -\frac{q_u}{R} \quad (4)$$

Here q_u is the *isosteric* heat of adsorption, a differential quantity which varies with the degree of surface coverage, hence also with the amount

REFERENCES

adsorbed v . Plots of q_{st} vs. v , commonly referred to as 'heat curves', are useful in determining the thermodynamic functions of the system, in characterizing the nature of the adsorbent surface and in estimating the degree of lateral interaction.

Isobars, plots of amount adsorbed at constant pressure as a function of temperature, may be interpolated from isotherms or measured directly but they have little utility in physical adsorption studies.

The heat of adsorption may also be measured calorimetrically and, since the amount adsorbed is also required, the adsorption isotherm is conveniently measured at the same time. In calorimetric work a finite amount of gas is admitted to the adsorbent in the calorimeter and so the heat measured is an integral quantity. In practice, however, the increments of gas admitted may be made so small that the heat measured closely approximates the differential quantity. Good agreement between isosteric and calorimetric heats of adsorption has been secured, particularly in recent work, giving grounds for confidence in both types of measurement.

Given the free energy change as a function of v (i.e. an isotherm) and the heat of adsorption as a function of v , the change in entropy accompanying adsorption may also be obtained as a function of the amount adsorbed (equation 1). These thermodynamic quantities may be complemented by calorimetrically determined values of the heat capacity of the adsorbed film.

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* The publishers have used journal abbreviations as given in *World List of Scientific Periodicals*: Butterworths, London, 1962.

PHYSICAL ADSORPTION FORCES

INTRODUCTION

THE forces giving rise to adsorption are no different from those involved in any other interatomic or intermolecular interaction phenomenon, but there are problems of special interest because the atoms of the solid are affected by the fact that they participate in the structure of the solid. The interactions between an atom or molecule and a solid surface are electromagnetic in origin, involving the electrons and nuclei of the system, the state of which is determined by quantum mechanics. When the equilibrium charge distribution is such that there is no transfer or sharing of electrons among the participating atoms and the individuality of the interacting species is thus maintained, the forces are said to be physical. Such forces are associated with physical or van der Waals adsorption. In principle then, the interaction between an atom or molecule and a solid surface can be found by determining the quantum mechanical state of the system of an atom or molecule and a solid, and then calculating the electromagnetic interactions. Since far simpler problems cannot be dealt with exactly, it is necessary to resort to various approximations.

The physical interaction between an atom or molecule and a solid surface is due to the attractive van der Waals forces which, following Margenau¹, may be defined simply as the forces which give rise to the constant a in van der Waals' equation, and the repulsive forces which arise when atoms come close enough together to allow interpenetration of the electron clouds.

Attractive forces pertinent to physical adsorption may be divided into several categories. If the adsorbed atom or molecule possesses no permanent dipole or multipole moment, then the attractive interaction with the solid surface is due to non-polar dispersion forces only, unless the solid itself has an external electric field, as, for example, in the case of an ionic crystal. In this latter case the field of the adsorbent will induce electric moments in the adatom*, producing an interaction in addition to the dispersion forces. If the adsorbed atom or molecule has multipole moments of its own, there will be additional

* The term adatom or admolecule is used to designate an adsorbed atom or molecule.

DISPERSION FORCES

interactions with the adsorbent due to: (a) charge distributions induced in the adsorbent, and (b) interactions of these moments with any permanent field of the solid. Although it is undoubtedly artificial to separate the above interactions, it is convenient to do so, both for ease in conception and simplicity in computation.

DISPERSION FORCES

Dispersion Forces between Pairs of Molecules

For a better understanding of the general procedures involved, it is profitable to examine first the nature of dispersion forces between a pair of atoms or molecules. Consider an inert gas atom in the ground state. The charge distribution is spherically symmetrical and therefore the atom possesses no permanent dipole or multipole moment and thus no external field. The kinetic energy of this state is not zero, as the atom has zero-point energy and possesses instantaneous dipole and multipole moments. The instantaneous moments induce in any neighbouring atom resonant moments which are in phase with those of the first atom and there is thus a force of attraction between the atoms. This resonance has been elegantly described by Lennard-Jones² as due to 'a sympathetic fluctuation of the electron space clouds of the two atoms, which produces in the atoms effective dipoles tending to move more in phase than out of phase'. These forces are known as dispersion forces on account of their relationship, noted by London³, to optical dispersion.

The usual quantum mechanical calculation of the dispersion energy makes use of a straightforward perturbation or variational technique. In all but the simplest cases the wave function of the individual atoms is taken as that for a set of isotropic harmonic oscillators or, as London⁴ has put it, an 'orchestra of periodic dipoles'. It is significant that the unperturbed wave function is usually not anti-symmetrized in the electron coordinates, which means that the results are valid only as long as the atoms are far apart, usually farther apart than the equilibrium separation, the distance of principal interest in adsorption studies. If the individual atoms possess no resultant angular momentum and the perturbation is taken as the interaction between instantaneous dipoles, the first-order perturbation is zero and it is the second-order perturbation which is the dispersion energy. The result under these conditions is the well known expression

$$E = -C/r^6 \quad (1)$$

where r is the distance between the atoms and C is a constant. E is often referred to simply as the dispersion energy.

The value of C in the perturbation approach outlined above depends on the energy levels of the atoms and the quantum mechanical oscillator strengths, which in turn depend on the transition probabilities between the electronic states. Actually, as far as interactions of this type are concerned, atoms frequently behave as isotropic oscillators with a single frequency corresponding to the characteristic optical dispersion frequency. Under these conditions, London³ derived the expression

$$C_L = \frac{3}{2} \alpha_1 \alpha_2 \frac{h \nu_1 \nu_2}{\nu_1 + \nu_2} \quad (2)$$

where C_L refers to this particular expression for C , α_1 and α_2 are the polarizabilities of the two atoms, ν_1 and ν_2 are the corresponding characteristic frequencies, and h is Planck's constant. Since $h\nu_1$ and $h\nu_2$ are often approximately equal to the ionization energies I_1 and I_2 of the atoms, C_L is sometimes written as

$$C_L = \frac{3}{2} \alpha_1 \alpha_2 \frac{I_1 I_2}{I_1 + I_2} \quad (3)$$

By applying a variational method Slater and Kirkwood⁵ obtained the expression

$$C_{SK} = \frac{3eh}{4\pi m^{1/2}} \frac{\alpha_1 \alpha_2}{(\alpha_1/N_1)^{1/2} + (\alpha_2/N_2)^{1/2}} \quad (4)$$

where e and m are the charge and mass of the electron, and N_1 and N_2 represent the number of electrons in the outer shells of the atoms. This treatment neglected the inner electrons. Kirkwood⁶ let N_1 and N_2 be the total number of electrons in the atoms, but this approach clearly overweighted the inner electrons. Hellmann⁷ and Buckingham⁸ introduced summations over the sub-shells; unfortunately the information needed to make use of these results is rarely available. Perhaps the most reasonable interpretation, suggested by Margenau¹, is that the values of N play the same role as quantum mechanical oscillator strengths and might best be regarded as empirical constants.

Another expression for C which has been used, particularly in calculations of interactions of molecules with solid surfaces, is the

Kirkwood-Müller⁹ equation which involves the magnetic susceptibilities χ_1 and χ_2 of the atoms:

$$C_{KM} = 6mc^2 \frac{\alpha_1 \alpha_2}{(\alpha_1/\chi_1) + (\alpha_2/\chi_2)} \quad (5)$$

where m is the mass of the electron and c is the velocity of light. Actually this equation cannot be expected to be precise, as Margenau¹ has noted, since the mechanism which gives rise to dispersion forces is quite different from that which is significant in the interaction of electrons with magnetic fields. A refined form of equation (5) which gives closer agreement with experimental results and includes electron correlation terms, has been developed by Salem¹⁰.

Derivations of equations (1) to (5) may be found in Margenau¹. Other summaries of particular value have been given by London⁴, and more recently by Hirschfelder, Curtiss and Bird¹¹ and by Pitzer¹².

Equation (1) arises from dipole-dipole interactions only. If dipole-quadrupole and quadrupole-quadrupole interactions are included, it is found that

$$E = -C/r^6 - C'/r^8 - C''/r^{10} \quad (6)$$

where the constants C' and C'' can in principle be calculated from the wave functions of the interacting species. Calculations have been carried out only for a few atoms (see Hirschfelder, Curtiss and Bird¹¹ for a review) and for harmonic oscillators^{13,14,15} giving expressions analogous to equation (2). Kiselev and co-workers¹⁶ have obtained equations for C' and C'' analogous to the Kirkwood-Müller equation (5). The contribution to E from the terms in equation (6) clearly depends on the separation, r , between the atoms in question. At the van der Waals minimum separation between two hydrogen atoms, Margenau¹ estimated that the dipole-quadrupole term amounts to about one-half, and the quadrupole-quadrupole term one-seventh, of the dipole-dipole term. For helium at the van der Waals minimum the dipole-quadrupole term was about one-quarter the dipole-dipole term. Using equation (6) to calculate heats of adsorption of a variety of gases on graphite, Kiselev and collaborators¹⁶ estimated that dipole-quadrupole term contributed of the order of 10 per cent and the quadrupole-quadrupole term of the order of 1 per cent to the total value of the dispersion interaction.

A problem of some importance is to find a value for C_{12} between unlike atoms 1 and 2, if values of C_{11} and C_{22} , the appropriate constants