

P. L. Huyskens · W. A. P. Luck
T. Zeegers-Huyskens (Eds.)

Intermolecular Forces

**An Introduction
to Modern Methods and Results**



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Preface

The study of intermolecular forces began over one hundred years ago in 1873 with the famous thesis of van der Waals. In recent decades, knowledge of this field has expanded due to intensive research into both its theoretical and the experimental aspects. This is particularly true for the type of very strong cohesive force stressed in 1920 by Latimer and Rodebush: the hydrogen bond, a phenomenon already outlined in 1912 by Moore and Winemill. Hydrogen bonds exert a profound influence on most of the physical and chemical properties of the materials in which they are formed. Not only do they govern viscosity and electrical conductivity, they also intervene in the chemical reaction path which determines the kinetics of chemical processes.

The properties of chemical substances depend to a large extent on intermolecular forces. In spite of this fundamental fact, too little attention is given to these properties both in research and in university teaching. For instance, in the field of pharmaceutical research, about 13 000 compounds need to be studied in order to find a single new product that can be successfully marketed. The recognition of the need to optimize industrial research efficiency has led to a growing interest in promoting the study of intermolecular forces. Rising salary costs in industry have encouraged an interest in theoretical ideas which will lead to tailor-made materials.

These developments require increased cooperation between fundamental research and industrial development and are facilitated by work in fields such as computer simulation of chemical and physical properties.

The research workers who in the future will bridge the gap between fundamental and applied research are the cream of today's university students. In order to bring the most recent fundamental and applied research in the field of intermolecular

forces to these students, an intensive Erasmus course was organised at the University of Leuven, Belgium in 1989. Lectures on the many aspects of this topic were given by specialists from Belgium, Germany and the Netherlands (where van der Waals was born) and other countries. This book contains these lectures adapted for publication and extended for a larger public by several supplementary articles. We hope that this book will not only promote the status of intermolecular forces for advanced students and researchers but also influence university teachers to pay more attention in their courses to the fruitful field of intermolecular forces and their role in determining the properties of materials.

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CHAPTER I

Intermolecular Forces

Th. Zeegers-Huyskens and P. Huyskens

No fundamental difference exists between cohesion forces and chemical bonds. They chiefly originate from coulombic interactions between charged particles. Repulsion forces are only important when the distance between the atoms falls below the sum of the van der Waals radii. *Van der Waals* forces are cohesive attractions between molecules that are already active at long interdistances. They result from interactions between permanent, induced or temporary electric dipoles. The last are called "dispersion forces". *Specific interactions* are cohesion forces that are only effective when so called specific sites of both molecules come into contact. In fact, specific interactions, as for instance hydrogen bonds, are short-range site-bounded cohesion forces that considerably weaken a given chemical bond of one of the partners. In the $A-H \cdots B$ hydrogen bond, the interdistance between the proton and the nearest nucleus of B is much shorter than the sum of the van der Waals radii, the distance $A-H$ is larger than in the unperturbed molecule and the cohesion energy is intermediate between that of pure dispersion forces in the liquid state and the energy of normal chemical bonds. Hydrogen bonds appear as an intermediate step of the transfer of a proton from AH to B. In this transfer a new chemical bond BH^+ is formed. H-bonds already share two characteristics of the chemical bonds: the stoichiometry and the directionality. In contrast their lifetime is very short. These characteristics are also those of the so-called $n-\sigma$ EDA bonds. The energy of a hydrogen bond is governed by the difference in proton affinity of B and the anion A^- . A quantitative expression is proposed.

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1 Cohesion Forces

1.1 Cohesion Forces and Chemical Bonds

Cohesion forces and chemical bonds govern the distances between the nuclei.

As a rule chemical bonds or valence forces can be defined as those that are preserved when low-molecular substances are brought in the gas phase. At normal pressures, cohesion forces in the gaseous state are very weak and their contribution to the total energy of the system is small. To a good approximation the cohesive energy of low-molecular substances in the liquid or in the solid state is therefore equal to the energy needed to vaporize them.¹

The existence of cohesion forces was for the first time envisaged by Laplace in 1806 in order to explain the phenomena of capillarity.

In fact, no fundamental differences exist between cohesion forces and chemical bonds. They both chiefly originate from the coulombic interactions between charged particles, electrons and nuclei, present in the atoms. When interactions between charges of different sign predominate, the resulting effect is an attraction. Repulsion occurs in the opposite case.

¹ Carboxylic acids constitute an exception because they are still strongly H bonded in the saturated vapor phase

1.2 Repulsion Forces

In general, the repulsion forces become only important when the distances between the nuclei fall below a given limit. The order of magnitude of this limit is the Ångström ($1 \text{ Å} = 0.1 \text{ nm}$). For atoms belonging to different molecules this limit is the sum of the so-called Van der Waals radii of the atoms. The Van der Waals radius of a given atom is the halve of the shortest distance observed in crystals between the nuclei of atoms of the same nature belonging to different molecules.

Table 1. Van der Waals radii $r_{\text{vdw}}/\text{Å}$ of atoms

				H	1.20	He	1.30
N	1.50	O	1.40	F	1.35	Ne	1.40
P	1.90	S	1.85	Cl	1.80	Ar	1.70
As	2.00	Se	2.00	Br	1.95	Kr	1.80
Sb	2.20	Te	2.20	I	2.15	Xe	2.05

CH_3 and CH_2 groups: 2.00 Å from the center of the carbon atom via the H-atoms.

Thickness of aromatic ring: $2 \times 1.85 \text{ Å}$.

In a chemical bond the internuclear distance is markedly lower than the sum of the Van der Waals radii. For instance, in H_2 the $\text{H}\dots\text{H}$ distance is 0.74 Å instead of 2.40 Å , in O_2 1.21 Å instead of 2.80 Å , and in N_2 1.10 Å instead of 3.00 Å .

1.3 Van der Waals Forces and Specific Interactions Between Molecules

When the interdistance between the nuclei is larger than the sum of the Van der Waals radii of the atoms, the interaction results as a rule in an attraction.

Such interactions were considered for the first time in 1873 by Van der Waals in order to explain the deviations of gases from the ideal behavior. According to Van der Waals, the pressure exerted by a gas on the walls of a vessel is lower than that predicted by the ideal law because the molecules that collide with the wall are somewhat retained by the attraction they undergo from the other molecules in the bulk of the gas:

$$p = \left(\frac{nRT}{V - nb} \right) - a \left(\frac{n^2}{V^2} \right) \quad (1)$$

The pressure correction and the “a” factor of Van der Waals are thus due to some remanent cohesion energy in the gas phase.²

The attraction forces that are at the origin of this cohesion are called “Van der Waals” forces. They are stronger in liquids or in solids owing to the shorter distances between the nuclei.

One can thus define the Van der Waals forces as cohesive attractions between molecules that are already active at long interdistances between atoms.

Besides the Van der Waals forces there exist cohesion forces acting at short distances, namely the hydrogen bonds and the charge transfer (EDA) bonds. These short-range forces are also called “specific” cohesion forces because they require the contact between given specific sites of the molecules of the partners.

1.4 Origin of the Van der Waals Cohesion Energies. Their Quantitative Expression in Gases

From a quantitative point of view, Van der Waals forces between gaseous molecules correspond to interactions between electric dipoles. One may distinguish three kinds of electric dipoles in molecules:

1.4.1 Permanent Dipoles μ^0

Molecules have a permanent dipole moment when in the unperturbed state, the center of charge of the nuclei does not correspond with that of the

Table 2. Dipole Moments of molecules μ^0 in the gaseous phase in Debye and SI units (Cm) [1]

	Debye	10^{-30} Cm		Debye	10^{-30} Cm
<i>n</i> -Butane	0.00	0.00	Pyridine	2.23	7.44
<i>n</i> -Pentane	0.00	0.00	Cyclohexanone	2.90	9.67
<i>n</i> -Hexane	0.00	0.00	Acetone	2.90	9.67
Cyclohexane	0.00	0.00	Nitroethane	3.20	10.7
Benzene	0.00	0.00	Propionitrile	3.50	11.7
Toluene	0.36	1.20	Dimethylacetamide	3.70	12.3
Triethylamine	0.78	2.60	Dimethylformamide	3.90	13.0
Hydrogen chloride	1.10	3.67	Dimethylsulfoxide	3.92	13.1
Diethylether	1.21	4.04	Propylenecarbonate	4.98	16.6
1,2-Dichloroethane	1.39	4.64	Lithium fluoride	6.40	21.3
Dichloromethane	1.58	5.27	Lithium chloride	7.09	23.6
Tetrahydrofurane	1.76	5.87	Sodium chloride	9.06	30.2
Methylacetate	1.80	6.00	Potassium chloride	10.70	35.7
Water	1.84	6.13			

² To a first approximation, for mono-atomic gasses the b parameter is related to the crystallographic Van der Waals radius and to Avogadro's number by the relation $b = (16\pi N/3)r_{vdw}^3$

electrons. Permanent moments of neutral molecules range from 0 to 15 Debye (1 Debye = 3.3356×10^{-30} Cm).

1.4.2 Induced Dipole Moments

These are caused by the displacements of electrons and nuclei under the influence of an external electric field E . The induced moment μ^{ind} is proportional to the applied field. The proportionality coefficient is the polarizability α of the molecule:

$$\mu^{\text{ind}} = \alpha E \quad (2)$$

The polarizability can be calculated from the refractive index n and the density ρ of the substance according to the Lorenz–Lorentz equation:

$$\alpha = \frac{3}{4\pi N} \left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{M_B}{\rho} \quad (3)$$

M_B is the molecular weight of the molecule B and N Avogadro's number. Polarizabilities are of the order of 10^{-24} cm³. They are rather unsensitive to changes in temperature or density. They depend on the frequency of the alternating field according to the equation:

$$\alpha_v = \frac{a_B}{v_B^2 - v^2} \quad (4)$$

where a_B and v_B are characteristic constants of the substance. v_B is called “dispersion” frequency and is of the order of 10^{15} s⁻¹.

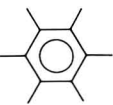
Table 3. Dispersion frequencies v_B/s^{-1} of various molecules

Gases		Liquids	
He	5.9×10^{15}	Water	3.17×10^{15}
Ne	5.2×10^{15}	Cyclohexane	3.24×10^{15}
Ar	3.5×10^{15}	Diethylether	2.37×10^{15}
Xe	2.8×10^{15}	Benzene	3.13×10^{15}
H ₂	4.0×10^{15}	Methanol	3.34×10^{15}
N ₂	4.1×10^{15}	Ethanol	3.54×10^{15}

To a good approximation the polarizability of a given molecule can be calculated from group contributions α_g given in Table 4.

$$\alpha = \sum \alpha_g \quad (5)$$

Table 4. Group contributions $\alpha_{\text{gD}}/10^{-25} \text{ cm}^3$ for the polarizability (Na-line)

—H	3.9	—NO ₂	19.7	≡CH	13.7
—F	4.5	—CH ₃	22.4	—C≡C—	27.1
—Cl	22.1	—CH ₂	18.4	—C=C—C=C—	57.7
—Br	33.1	—CO	22.0	≡N	10.4
		H			
—I	52.9			—S—S—	60.8
—O—H	9.6	—CO	23.5	—C=C—	25.6
		O			
—S—H	3.2				9.8
				—C—	
—NH ₂	16.4	—O—	6.7		
—CN	20.7	—S—	30.0		80.5
		=SO	32.8		
		=NH	13.7		

1.4.3 Temporary Moments

The dispersion frequency is directly related to the motions of the electrons. During a time shorter than the inverse of the dispersion frequency ν_B , an atom or a molecule (even apolar) exhibit temporary moments due to the motions of the electrons.

Equations were derived for the various interaction energies in the gas phase. Interactions between the permanent dipole moments μ_A^0 of the molecule A and μ_B^0 of the molecule B separated by a distance r in the gas phase provoke a lowering of the molar energy calculated by Keesom (1912):

$$\varepsilon_{\mu_A^0 \mu_B^0} = - \left(\frac{2N^2}{3RT} \right) \frac{\mu_A^{02} \mu_B^{02}}{r^6} \quad (\text{Keesom}) \quad (6)$$

R is the gas constant and T the absolute temperature. Debye (1920) calculated the molar energy of interaction between the permanent dipole μ_A^0 and the polarizable molecule B at a distance r :

$$\varepsilon_{\mu_A \alpha_B} = - \mu_A^{02} \alpha_B N / r^6 \quad (\text{Debye}) \quad (7)$$

A quantitative expression for the interaction between temporary moments ("dispersion forces") was derived by London (1930):

$$\varepsilon_{\alpha_A \alpha_B} = - \frac{3N}{2} \left(\frac{h\nu_A^0 \nu_B^0}{\nu_A^0 + \nu_B^0} \right) \frac{\alpha_A^0 \alpha_B^0}{r^6} \quad (\text{London}) \quad (8)$$

where α_A^0 and α_B^0 are the polarizabilities in a permanent field ($v = 0$). h is Planck's constant (6.6256×10^{-34} Js).

The dispersion frequencies of the various substances are all of the same order of magnitude. Furthermore, at a given temperature and under a given pressure the molar volume of gases (and, thus, the mean interdistances between the molecules) is independent of the nature of the gas. We may therefore conclude that the cohesion energy of gases is governed by the two molecular characteristics: the polarizability and the permanent dipole moment.

1.5 Dispersion Forces in Liquids

In apolar substances only dispersion forces are responsible for the cohesion. According to London, the cohesive energy per unit volume originating from the dispersion forces in the gas phase is directly proportional to the square of

Table 5. Molar energy of vaporization ΔU_{vap} , refractive index n_D^{25} , molar volume \bar{V} , polarizability α , ratio $k = \Delta U_{\text{vap}}/\alpha^2$ of apolar liquids at 25°C [2]

	ΔU_{vap} kJmol^{-1}	n_D^{25}	\bar{V} $\text{cm}^3\text{mol}^{-1}$	α 10^{-24}cm^3	k 10^{52}Jcm^{-3}
2,2-Me ₂ Propane	19.37	1.3417	118.2	9.86	2.36
<i>n</i> -Pentane	23.95	1.3560	116.1	10.05	2.75
<i>n</i> -Hexane	29.07	1.3735	131.6	11.90	2.70
<i>n</i> -Heptane	34.07	1.3861	147.5	13.74	2.67
<i>n</i> -Octane	39.01	1.3957	163.5	15.56	2.64
2,2,4,4-Me ₄ -Pentane	35.68	1.4032	179.2	17.34	2.12
<i>n</i> -Nonane	43.96	1.4037	179.6	17.40	2.61
<i>n</i> -Decane	48.89	1.4085	195.9	19.18	2.61
2,2,3,4-Me ₄ -Pentane	38.36	1.4111	174.5	11.18	2.26
SiCl ₄	27.60	1.4151	115.1	11.43	2.46
<i>n</i> -Undecane	53.86	1.4154	212.2	21.03	2.59
BCl ₃	20.60	1.4173	88.1	8.79	2.36
<i>n</i> -Dodecane	58.81	1.4198	228.6	22.92	2.51
2,3,3,4-Me ₄ -Pentane	39.37	1.4204	170.8	17.15	2.29
2,2,3,3-Me ₄ -Pentane	38.69	1.4218	174.3	17.55	2.19
Cyclohexane	29.16	1.4248	108.8	11.08	2.62
<i>n</i> -Tridecane	63.75	1.4272	244.9	24.93	2.51
<i>n</i> -Tetradecane	68.69	1.4284	261.3	26.67	2.53
<i>n</i> -Pentadecane	73.67	1.4297	277.7	28.42	2.53
<i>n</i> -Hexadecane	78.61	1.4327	294.1	30.28	2.52
<i>n</i> -Heptadecane	83.78	1.4351	310.4	32.11	2.52
GeCl ₄	31.40	1.4592	116.8	12.68	2.23
CCl ₄	30.30	1.4610	97.8	10.64	2.63
1,4-Et ₂ -Benzene	50.00	1.4946	156.5	18.08	2.39
1,3,5-Me ₃ -Benzene	45.00	1.4973	139.2	16.15	2.39
Benzene	31.40	1.4990	89.4	10.40	2.60
SnCl ₄	37.50	1.5128	117.6	14.01	2.25
AsCl ₃	33.90	1.6006	84.2	11.43	2.19
CS ₂	25.50	1.6253	60.4	8.47	2.14

the polarizability. As said before, the polarizabilities are little sensitive to changes in the density. On the other hand, in contrast to the gas phase, the molar volume of the liquid depends on its nature. Furthermore, in an homologous series we expect that the cohesive energy per unit volume will tend to some limiting value within series. These considerations lead to the following correlation between the molar energy of vaporization $\bar{\Delta}\bar{U}_{\text{vap}}$ and the polarizability of apolar substances [2]:

$$\bar{\Delta}\bar{U}_{\text{vap}} = k\alpha^2/\bar{V} \simeq k'\bar{V} \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right)^2 \quad (9)$$

where \bar{V} is the molar volume and n the refractive index for the sodium line (taken to estimate to a first approximation the static polarizability).

These correlations were tested for some thirty apolar liquids. One observes a reasonable constancy of $k = 2.45 \pm 0.18 \times 10^{49} \text{ kJcm}^{-3} \text{ mol}^{-1}$ (and $k' = 3.97 \pm 0.29 \text{ kJcm}^{-3} \text{ mol}^{-1}$).

1.6 Contribution of Cohesion Forces other than Dispersion Forces in the Molar Energy of Vaporization of Liquids

The contribution of the other cohesion forces (dipole–dipole interactions or H Bonds) in the total molar energy of cohesion $\Delta\bar{U}_{\text{residual}}$ can be calculated from the molar energy of vaporization and from the refractive index and the molar volume by means of the expression derived from Eq. (9):

$$\bar{\Delta}\bar{U}_{\text{residual}} = \bar{\Delta}\bar{U}_{\text{vap}} - 3.97 \text{ kJ cm}^{-3} \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right)^2 \bar{V} \quad (10)$$

Examples are given in Table 6.

The first part of the list contains polar liquids without H-bonds. The intervention of dipole–dipole interactions in the cohesion energy is evident. To a rough approximation $\bar{\Delta}\bar{U}_{\text{residual}}$ is proportional to the dipole moment per unit volume. One finds:

$$\bar{\Delta}\bar{U}_{\text{residual}} \simeq 622 \pm 102 \text{ kJD}^{-1} \text{ cm}^3 \mu^0/\bar{V} \quad (11)$$

However, a proportionality between $\bar{\Delta}\bar{U}_{\text{residual}}$ and μ^{04}/\bar{V}^2 that should be expected on the basis of the expression for the gas phase is not observed.

For the alcohols of Table 6 two important remarks have to be made: first, the residual molar cohesion energy is markedly larger than the values expected on the basis of Eq. (11). For methanol one finds 28.3 kJmole^{-1} instead of 21.8 kJmole^{-1} and for 1-hexanol one finds 28.2 kJmole^{-1} while Eq. (11) yields