Topics in Current Chemistry

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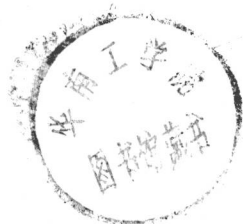Weights by Light Scattering

Inorganic and Physical Chemistry

77 Topics in Current Chemistry

Fortschritte der Chemischen Forschung

Inorganic and Physical Chemistry

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This series presents critical reviews of the present position and future trends in modern chemical research. It is addressed to all research and industrial chemists who wish to keep abreast of advances in their subject.

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Volume 1
R. Reisfeld, C. K. Jørgensen
Lasers and Excited States of Rare Earths
1977. 9 figures, 26 tables. VIII, 226 pages
ISBN 3-540-08324-3

The authors discuss both numerous spectroscopic questions, including the influence of the neighbour atoms on positions, and intensities of transitions in trivalent Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb and other effects of chemical bonding in vitreous and crystalline solids, as well as the parameters determining the applications in lasers, such as the radiative and non-radiative transitions probabilities, the strategy for suppressing radiationless processes competing with luminescence, and the energy transfer from trivalent cerium, the uranly ion, vanadate, tungstate, ions of thallium, lead and bismuth isoelectronic with mercury atom (and from many other species) to the rare earth. In a final chapter, general questions of radiation from opaque objects, communications, geodesy and astrophysics are discussed, and the use of neodymium glass lasers for initiating nuclear fusion reviewed. Many new suggestions are presented in this novel interdisciplinary field.

Volume 2
R. L. Carlin, A. J. van Duyneveldt
Magnetic Properties of Transition Metal Compounds
1978. 149 figures, 7 tables. XV, 264 pages
ISBN 3-540-08584-X

This book introduces chemists and physicists to magnetic ordering phenomena, Chemists have long been interested in magnetic interactions in clusters, but have shied away from the cooperative phenomena that have always fascinated physicists. Part of the reason for this is that the most remarkable phenomena occur at low temperatures, a region where many chemists have only recently started making measurements. This work starts with a study of paramagnetisms, and shows the specific heat results are as valuable a magnetic measurement as a susceptibility. Emphasized throughout is the valuable information to be obtained by measuring single crystals, rather than powders. The subject of paramagnetic relaxation is also introduced. Numerous illustrative examples from literature are cited throughout. The book concludes with an extensive literary survey of both the single-ion properties of the iron-series ions, and ten interesting examples of magnetic systems to which the principles introduced in the beginning of the book have been applied.

Volume 3
P. Gütlich, R. Link, A. Trautwein
Mössbauer Spectroscopy and Transitions Metal Chemistry
1978. 160 figures, 19 tables, 1 folding plate.
X, 280 pages
ISBN 3-540-08671-4

The book is directed to chemists, physicists and other scientists and is suitable for beginners wishing to acquire an understanding of the method of Mössbauer spectroscopy. It should also be particularly apreciated by the advanced scientists who wishes to apply the method to compounds and alloys of transition metals. In describing numerous examples the authors demonstrate the kind of problems which may be solved using the Mössbauer effect technique. The chapters dealing with non-iron Mössbauer active transition elements include complete lists of references to original work on solid-state chemistry and physics. In the chapter on ^{57}Fe-spectroscopy the authors have shown various ways of chemical bond and molecular structure investigations in connection with quantum-chemical methods. The last chapter introduces the reader into a number of special applications of Mössbauer spectroscopy.

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Contents

Surface Energy of Solids

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List of Symbols

A	Surface area; a constant
A_m	Area of surface or interface per molecule
A, A_s, A_{sl}	Areas of vapor-liquid, vapor-solid, and liquid-solid interfaces
A_1	Combined area of grain boundaries
A_0, A_1	Surface areas of a large and a minute crystal
A_1, A_2, A_3	Areas of different crystal faces
a	The longer half-axis of an ellipse; lattice parameter
B	A constant
b	The shorter half-axis of an ellipse
C, C_1, C_2	Solubilities
$C.E.$	Cuticular energy
c	Depth or half-length of scratch
D	Grain diameter; diffusion coefficient
E	Modulus of elasticity; intensity of electrostatic field
E_0	Internal energy of a bar
E_1	Internal energy of a broken bar
e	Charge of an electron
F	Helmholtz free energy
F_o	Free osmotic energy
F_s	Free surface energy
f	Force; number depending on crystal structure
G	Shear modulus; arbitrary constant; temperature gradient
H	Amount of heat evolved
h	Planck's constant; half-thickness or thickness of a slice or a ribbon; depth of scratch
h_0	Initial depth of scratch
K	Modulus of compressibility; proportionality constant
k	Boltzmann's constant; coordination number of atoms in bulk; compressibility
k_s, k_v	Number of atoms in two-dimensional and three-dimensional unit cells
Δk	Number of broken bonds per atom
L	Length; thickness of a crystal
L_l, L_s	Heat of vaporization or sublimation
l	Length; length of a "roof"; variable length of a filament
l_0	Initial length of a filament
l_1, l_2	Edges of two cubes
M	Molecular weight; atomic mass
MW	Molecular weight
m	Mass of an atom; mass of hydrogen atom; mass
N	Number of atoms in unit cell; Avogadro number
n	Number of grain boundaries in a wire; number of molecules in unit volume
n_+, n_-	Number of cations or anions on unit area
P	Gas pressure
P_c	Capillary pressure
P_o	Vapor pressure above a plane surface
p_1, p_2	Pressure in gas, in liquid
Q	Heat content
Q_0, Q_p, Q_∞	Heat of solution of large and powdered solids, and solids with zero surface
q	Number depending on crystal structure; surface density of electric charge
q_0, q_1	Heat of solution of unit mass
R	Radius of curvature; gas constant
R_1, R_2	The principal radii of curvature
R_∞	Distance at which deformation becomes negligible

R	Radius of wires; distance from an atom or ion; cube root of molecular volume; radius of a void
r_0	Radius at the bottom of a groove; radius at zero time
r_1, r_2	Radius of wire before and after elongation
S. E.	Strain energy
T	Absolute temperature
T_b, T_m	Boiling and melting points
T_l	Melting point of plate of thickness l.
T_{mr}	Melting point of drop of radius r
T_t	Temperature of treatment
t	Time
U	Interatomic potential
U_l, U_s	Total surface energy of a liquid, a solid
u	Height of a ridge point
u_1, u_2	Displacement of neighboring atoms
V	Volume of unit cell; specific volume of a liquid; volume; molecular volume
V_1, V_2	Gas and liquid volumes
W	Load; breaking load
W_0	Equilibrium load on a filament
W_w	Breaking load of wires
$\mathfrak{W}$	Work of extending a rod
$\mathfrak{W}_f$	Fracture energy
$\mathfrak{W}_m$	Work spent on macroscopic deformation
w	Width; distance between two ridges
x	Variable depth of crack
Y	Plate thickness
Z	Valency of an ion; effective number of electrons per ion
α	Angle on a crystal surface; numerical constant; an angle
β	Contact angle at the edge of a solid
γ	Surface tension of a liquid
γ_c	"Critical surface tension"
γ_s	Specific surface energy or surface tension of a solid
γ_s^*	Specific free energy of an interface between UC and U vapor
γ_{sl}	Specific energy or tension of a liquid-solid interface
γ_{sv}	Surface tension of a solid in a foreign vapor
γ_1	Surface tension of a grain boundary
$\gamma_{12}, \gamma_{13}, \gamma_{23}$	Tensions along boundaries between fluids 1 and 2, 1 and 3, and 2 and 3
"γ"	Specific fracture energy
Δ	Thickness of a line on which f acts
δ	Thickness of surface layer; an angle
ϵ_0	Maximum strain
η	Viscosity
θ	Contact angle
θ_0	The characteristic (Debye) temperature
λ	Wave length of disturbances; heat of melting
$\lambda_1; \lambda_s$	Internal heat of vaporization, sublimation
ν	Number of free valence electrons per atom; Poisson's ratio
ξ	Cohesion of a solid
ρ, ρ_3	Density of a solid
ρ_1, ρ_2	Density of a gas, a liquid
σ_0	Average stress
σ_m	Local stress
τ	Thickness of surface layer
φ	Potential energy of a crystal

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φ	Work of removing an atom from its neighbor; work function; half the dihedral angle in a liquid medium; electric potential
φ_1	Energy of valency electrons at the Fermi level
ψ	Half the dihedral angle in a gas
ψ^*	Dihedral angle in a foreign vapor
Ω	Volume of a molecule or atom

I. Introduction

Only surface energy is mentioned in the title of this review, but surface tension also is considered in the following text. The dimensions of (specific) surface energy (ergs/cm^2 or joules/m^2 or g/sec^2) and of surface tension (dynes/cm or newtons/m or g/sec^2) are identical. For typical liquids, also the two absolute values are equal; for instance, the surface tension of water γ at room temperature is about 72 dyne/cm, and the (specific) surface energy is 72 erg/cm^2.

For typical solids, not only is the relation between surface tension and surface energy poorly understood, but also the very existence of these quantities questioned. In the following brief historical sketch, an attempt will be made to indicate why scientists felt it necessary or useful to introduce notions of surface tension and surface energy (γ_s) of solids into science.

Apparently, the first reference to γ_s or "superficial cohesion" of a solid is found in an Essay by Thomas Young[1]. The original does not contain illustrations, but Fig. 1 here represents the author's idea. A solid wall (S) is partly wetted by liquid L
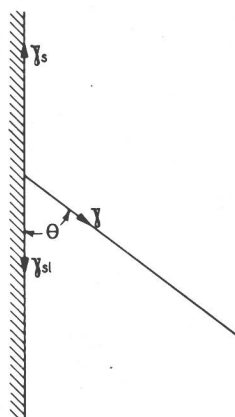
Fig. 1. The hypothetical balance of forces at the 3-phase line. The surface tension γ_s of the solid (shaded) is supposed to be equal to the sum $\gamma_{sl} + \gamma \cos \theta$; γ_{sl} is the tension along the liquid − solid interface, γ is surface tension of the liquid, and θ is the contact angle

while the vapor V is in equilibrium with both S and L. The angle occupied by L is θ. Along the boundary V/L the surface tension γ of the liquid acts; Young imagined an analogous surface tension γ_s to act along the boundary V/S and a tension γ_{sl} to act along the frontier L/S. To achieve equilibrium along the solid surface, it is necessary (if gravitation is neglected) to have the tension γ_s equal (and opposite) to the sum $\gamma_{sl} + \gamma \cos \theta$, or

$$\gamma \cos \theta = \gamma_s - \gamma_{sl} \tag{1}$$

The contact angle θ is always measured in the liquid.

As usual with Young, no attempt to prove his equation, and no attempt to justify the introduction of a tension of solid surfaces are made. A discussion of the

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above reasoning will be found in Section III.8 of this review, but one difficulty may be mentioned at once. Equation (1) was derived for the forces acting along the solid surface but it disregards the force normal to it. If γ tends to contract the V/L interface and if the vertical component $\gamma \cos \theta$ of this tension is believed to pull the solid atoms (present along the 3-phase line) downward, what effect has then the horizontal component $\gamma \sin \theta$? We would expect it to pull the above atoms out of the plane toward the right. Young[2] became aware of this component many years later but could only suggest that "the perpendicular attraction" is "counteracted by some external force holding the solid in its situation".

Another line of study was started by Quincke[3]: It has been found, experimentally, that the breaking load W_w of wires having different radii r could be expressed by the equation

$$W_w = mr^2 + nr, \tag{2}$$

m and n being empirical constants. Quincke's guess was, that the term nr represented the resistance offered by the surface tension of the wire. Hence, $nr = 2\pi r \gamma_s$ or $\gamma_s = n/2\pi$. At present it is generally admitted that the breaking stress (i.e., $W_w/\pi r^2$) of thin wires exceeds that of thicker samples because their microscopical structure is different. In particular, the act of drawing elongates many weak spots in the volume of the wire material.

If a thin solid plate contains an elliptic hole of the half-axes a (the longer one) and b, and the ellipse is oriented so that the longer axis is perpendicular to the direction of the tensile force, then the stress at the two ends of this axis is

$$\sigma_m = \left(1 + \frac{2a}{b}\right) \sigma_0 \tag{3}$$

σ_0 being the average stress caused by the external pull. Hence, the local stress concentration (equal to σ_m/σ_0) is greater the greater the ratio a/b. If the plate is extended by the above pull, this ratio decreases: an ellipse perpendicular to the tensile force may become parallel to it. Consequently, σ_m is lowered by drawing, and the average stress σ_0 must be raised to achieve that value of σ_m at which fracture proceeds. Equation (3) is the most probable explanation of Eq. (2) which, on this view, has no relation to any surface effect.

A relation between rupture phenomena and (specific) surface energy "γ" was postulated by Dupré[4] almost simultaneously with the hypothesis of Quincke. Let a cylindrical rod be broken in tension. After rupture, two new gas – solid interfaces of πr^2 each are present, r being the radius of the rupture surface. Consequently, the work of rupture ought to contain a term $2\pi r^2$ "γ". Dupré did not indicate how to separate this term from the main component of the work of rupture, which is the work required to extend the rod to its maximum elongation (or strain). The modern development of Dupré's ideas is reviewed in Section III.3. below.

Soon after Dupré's publication, Gibbs[5] pointed out that, whereas for liquids the work of extending the surface by dA cm^2 is identical with the work of creating a new surface of identical area, the two quantities are different for a solid. In fact,

it is difficult to imagine a method for expanding the surface area of a solid without altering the strain energy (or the stored elastic energy) of the bulk. The work required to create a new surface is evidently identical with that considered by Dupré.

Consequently, this kind of surface energy does not imply any superficial tension or tendency to contract. This was clear already to Gibbs and will be stressed again in Chapter V.

II. Theoretical Approach

1. General

Laplace's theory of capillarity (1805), confirmed for liquids in innumerable tests, in principle embraces solids also. It is based on the notion that each material point (or atom, or molecule) exerts an attractive force on all neighboring points but the intensity of this attraction decreases so rapidly when the distance between two points increases, that it is significant only when the above distance is negligible (the attraction is "sensible at insensible distances only"). This notion ought to be as valid for solids as for liquids. However, the visible or measurable consequences of the theory would be expected to be quite different for typical solids and typical liquids. In the latter, the mobility is so great that the equilibrium shape of liquid bodies is to a large extent determined by the capillary pressure existing at present and is not influenced by the pre-history of the specimen. It is possible to pour a Newtonian liquid from a cylindrical beaker into a vessel of a most intricate design, and then pour it back; no inspection of the resulting sample would permit us to detect the past contortion of the liquid.

The behavior of solids is, of course, quite different. Their present shape and their internal stresses and strains greatly depend on their pre-treatment. Thus we can measure the capillary pressure existing in a given liquid sample simply by measuring the shape of the sample in an external force field, such as one due to gravitation; but a determination of the capillary pressure in a solid is an almost impossible task. Chapter III deals with this difficulty.

Laplace could not express any opinion on the absolute values of the attraction assumed by him. At present, our knowledge of interatomic, interionic, and analogous forces is much greater than 170 years ago, and attempts to calculate surface energies and surface tensions are possible.

The usual procedure, however, does not follow Laplace's precedent, but rather uses Dupré's scheme. Consider a bar, of unit area cross section and containing $2n$ atomic layers perpendicular to the axis of the bar; n is a large number. Let the internal energy of the bar be E_0. If the bar is cut in two, so that each half contains n atomic layers, the energy of the system changes to E_1. One-half of the difference between the two energies is considered to be (specific) surface energy of the material, that is "γ" $= 0.5 \, (E_1 - E_0)$. The factor 0.5 appears, of course, because two rupture surfaces are formed by one act of separation.

The following Section II.2. is devoted to the attempts on calculating "γ" from fundamental atomic and molecular constants. In Section II.3., semi-empirical expressions for the surface energy of solids are briefly reviewed.

2. Basic Calculations

It is commonly agreed that E_1 is different from E_0 because the resultants of the forces acting on elementary particles (*i.e.* electrons, atoms, ions, etc.) near the rupture surface differ from those in the bulk of the material: the bulk is more symmetrical than the surface layer.

Three tiers of questions arise now.

1. What units must be considered? Is it enough to calculate the forces between molecules or must atoms, ions, nuclei, and electrons all be treated separately?

2. What displacements, as compared with the positions in the bulk, are permitted for each of the centers of force present in the surface layers?

3. Which of the many suggested laws of force (*i.e.*, what dependence of the attractive and repulsive forces on the distance between the particles concerned) should be chosen for the calculation?

From the above paragraph it is clear that very many different models may be subjected to calculation. The numerical results, naturally, vary from model to model (for a given real crystal), and at present it would be too risky to claim correctness for any of them. Consequently, only a few (mainly recent) examples of the approaches to the computation of "γ" are reviewed in this section, chiefly to indicate the unsettled state of affairs at present. Older theories and their numerical results may be consulted, for instance, in Ref.[6].

Inert Gases. The calculation of "γ" should be relatively straightforward for crystals of inert gases, in which only one kind of interaction may be expected. These crystals have a face-centered cubic structure. If each atom is treated as a point source of attractive and repulsive forces, only the forces between the nearest pairs of atoms are considered, the zero point energy is neglected, and no re-arrangement of atoms in the surface region is permitted, then the calculated "γ" still depends on the equation selected to represent the interatomic potential U.

A popular equation, often attributed to Lennard-Jones, is

$$U = C_1 r^{-12} - C_2 r^{-6} \tag{4}$$

r being the distance of an arbitrary point in space from the source of force, and C_1 and C_2 constants which usually are calculated from crystal properties and the second virial coefficients of the gases, assuming, of course, the validity of Eq. (4). With all the above restrictions, "γ" of the {100} faces of Ne, Ar, Kr, and Xe at 0 °K appeared to be 20.5, 45.0, 55.0, and 64.7 erg/cm² , respectively[7]. When, instead of (4), equation

$$U = be^{-kr} - cr^{-6} \tag{5}$$

was used, in which *b, k,* and *c* are constants to be determined from the heat of sublimation of the crystals at $0\,^\circ K$, and the viscosity and the second virial coefficients of the gases, the "γ" for the above four crystal faces became 19.9, 43.6, 55.5, and 64.7 erg/cm^2. If now the external atoms are allowed to rearrange themselves so as to lower the total energy as much as possible, the "γ" decreases by about 0.16 erg/cm^2 for neon and about 0.6 erg/cm^2 for xenon.

A later calculation[8], based on very similar notions, resulted, for instance, in a value of 40 erg/cm^2 (or 0.040 J/m^2) for the {100} face of argon, still apparently at $0\,^\circ K$.

If no re-arrangement of the peripheral atoms is permitted but, in addition to the forces between pairs of atoms, also those between one atom in one, and two atoms in the other fragment (of the initial ideal crystal) are computed, then the "γ" appears[9] to be lowered by 4–15% as compared with the values quoted above from Ref.[7].

The above calculations may be classified as static. The energy is altered by permitting the atoms to vibrate[10]. Let Φ be the potential energy of the crystal, and u_1 and u_2 the displacements of two neighboring atoms in the latter. The derivative $\partial^2/\Phi/\partial u_1 \cdot \partial u_2)$ is computed, that is, the effect of the simultaneous vibrations of other neighbor atoms is disregarded. The dependence of Φ on the mutual distance of two atoms is assumed to be that of Eq. (4). No change in the structure of the surface region is allowed below the melting point. With these (and other) approximations, the vibrational surface energy for the {100} surface of Ar, Ne, Kr, and Xe at $0\,^\circ K$ becomes 2.8, 2.7, 1.8, and 1.6 erg/cm^2, respectively; thus vibrations seem to contribute less than 10% to the value of "γ".

Ionic Crystals. Of the crystals consisting of two different atoms each, those of lithium hydride LiH are perhaps the simplest to deal with. In this system, four kinds of energy are taken into account[11], namely the kinetic energy of every particle, the energy of attraction between the nuclei and the electrons, that of the mutual repulsion between the nuclei, and that of the repulsion between the electrons. In the instance of LiH, there are only two different nuclei and only 4 electrons per molecule. Consequently, in the bulk of the crystal, only 5 variational parameters are important, namely the internuclear spacing, the ordinate of one orbital center (the Li nucleus being the origin of the co-ordinates), the ordinate of the other orbital center, and the two diameters of the orbitals. The analogous equations for the energies in the 3 ionic layers nearest to the rupture surface are more complicated; here 12 variational parameters are needed, namely six for the external, and six for the penultimate layer. There are 6 rather than 5 variables per each layer because the distance of the Li nucleus (serving as the origin of the co-ordinates) from the undisturbed third layer also is permitted to vary.

It is supposed that this displacement can occur only in the direction normal to the rupture surface, not parallel to the latter. When all the above distances are systematically varied until the minimum of the total interaction energy is reached, then the most probable position of all 6 centers of force is found. It appears that the distance between the Li nuclei in the outermost and the H nuclei in the second layer is smaller (by 0.00032 angstrom) than in the bulk of the crystal, and the distance between the H nuclei in the external and the Li nuclei in the penultimate layer is

(by 0.0016 angstrom) greater than in the bulk. The energy of these two layers exceeds that of two undisturbed layers in the crystal by 190 mJ/m^2 (or erg/cm^2).

The lattice energy (L.E.) of alkali halide crystals appears to be relatively easy to calculate, because the forces between the regularly spaced ions are chiefly of the Coulomb type. Thus 3 different models of the NaCl crystals yielded values of L.E. between 1.297 and 1.282 x 10^{-11} erg/molecule, that is, in a good agreement with each other. However, no such agreement is observed when the "γ" is computed for the same models[6]. Thus the earliest 9 estimates of the "γ" of the {100} face of NaCl at 0 °K gave[12] values ranging from 77 to 210 erg/cm^2.

The earliest theory (Born, Stern 1919) resulted in the simple equation

$$\text{``}\gamma\text{''} = 0.1173 \, z \, e^2/a^3 \text{ erg/cm}^2 \tag{6}$$

for the {100} face of NaCl; the numerical coefficient depends on the geometry of the crystal, z is the valency of each ion (i.e., $z = 1$ for NaCl), e is the charge of the electron, and a is the lattice parameter.

Zadumkin[12] considered 4 kinds of energy, namely the Madelung energy, the Born energy, the dispersion energy, and the zero-point vibrational energy. For the above crystal face, the values of these components at 0 °K appeared to be +367.6, −198.0, +50.5, and −7.3 erg/cm^2, respectively. Thus the expression for "γ" contained two positive and two negative terms. Naturally, the final result was very sensitive to the accuracy of each of them. The displacement of the ions caused by the proximity of the gas phase was disregarded in this computation.

More recently, the temperature dependence of the above vibrational component was studied[13]. Still for the {100} face of NaCl, the contribution of this component to the total surface energy, see Section II.3., was approximately −2 erg/cm^2 and to the free surface energy near − 16 erg/cm^2, both at 273 °K. No correction for the polarizability of the ions was employed.

Metals. A review of the published predictions of the "γ" of metals was published, for instance, in Ref.[14]. In that article, the idea of an uniform electron fluid in which metal cations are embedded is rejected; the electrons are concentrated in the spaces of the most intense electric field between the cations and thus form something like a second lattice. This remark seems to be disregarded by the later investigators.

According to two simultaneous hypotheses[15, 16], the principal component of the "γ" of simple metals (from lithium to aluminum) originates in the shift in the zero-point energy of the plasma models of the system when one perfect crystal is broken into two separate crystals. Some simplifications and arbitrary assumptions lead finally to the relation

$$\text{``}\gamma\text{''} = Cr^{-2.5} \tag{7}$$

C is a universal constant (calculable from the model) and r is the density parameter equal to $r = (3/4 \pi)^{1/3} (V/N\nu)^{1/3}$; V is the volume of the unit cell which contains N atoms, and each atom contributes ν "free" valence electrons to the collective motion. Because the actual crystal structure is disregarded, only one value of "γ" is obtained for each metal. For lithium, for instance, "γ" seems to be 490 erg/cm^2 and