

Contents

Physical Data, Notation and Online Materials

xxi

1 Preamble

- 1.1 Introduction
- 1.2 Atomic nature of matter
- 1.3 States of matter
- 1.4 Crystalline and amorphous solids
- 1.5 Isomorphism and polymorphism
- 1.6 Solid-state transitions
 - 1.6.1 Sharp transitions
 - 1.6.2 Gradual transitions
 - 1.6.3 Entropy of transition and the Boltzmann equation
 - 1.6.4 Thermodynamic properties at transition points
- 1.7 Liquid crystals
- 1.8 Classification of solids
 - 1.8.1 Covalent solids
 - 1.8.2 Molecular solids
 - 1.8.2.1 Hydrogen-bonded solids
 - 1.8.3 Ionic solids
 - 1.8.4 Metallic solids
 - 1.8.5 Comments on the classification of solids

References 1

Problems 1

2 Covalent Compounds

- 2.1 Introduction
- 2.2 Black-body radiation
- 2.3 Planck's quantum theory
- 2.4 Heat capacity
- 2.5 Wave-particle duality
 - 2.5.1 Photoelectric effect
 - 2.5.2 De Broglie equation
 - 2.5.3 Electron microscopy
- 2.6 Atomic spectra
- 2.7 Heisenberg's uncertainty principle
- 2.8 Wave mechanics of particles

1

1

2

3

6

10

12

13

14

16

18

19

22

22

22

22

23

24

24

26

26

29

29

30

32

33

34

34

36

37

37

38

40

2.9	Born's interpretation of the wavefunction	41
2.9.1	Normalization	42
2.9.2	Orthogonality and orthonormality	42
2.10	Particle-in-a-box: quantization of translational energy	43
2.10.1	Tunnelling	47
2.10.1.1	Scanning probe microscopy	48
2.10.1.2	Tunnelling in electron transfer reactions	49
2.10.2	Boxes of higher dimensions	50
2.10.3	Vibrational motion	51
2.10.4	Rotational motion	53
2.11	The hydrogen atom	55
2.11.1	The angular equations	57
2.11.2	The radial equation	58
2.11.3	The complete wave equation	62
2.12	Quantum numbers	64
2.12.1	Angular momentum and spin	65
2.12.2	Pauli's exclusion principle	66
2.13	Atomic orbitals	66
2.13.1	Ionization energy	66
2.13.2	Atom shells	68
2.13.2.1	Selection rules for atoms	69
2.13.3	Radial functions and size	69
2.13.4	Angular functions and shape	70
2.13.4.1	<i>s</i> Orbitals	70
2.13.4.2	<i>p</i> and <i>d</i> Orbitals	70
2.13.5	Screening constant and effective nuclear charge	74
2.14	Aufbau principle	74
2.15	Multi-electron species	77
2.16	Valence-bond theory	78
2.16.1	Homonuclear diatomic molecules	78
2.16.2	Heteronuclear diatomic molecules	80
2.16.3	Other molecular species	82
2.17	Molecular orbital method: homonuclear species	82
2.17.1	Variation principle	83
2.17.1.1	Hydrogen molecule-ion and hydrogen molecule	85
2.17.1.2	Orbital symmetry	86
2.17.1.3	Heteronuclear species	87
2.17.1.4	Nitrogen and oxygen molecules	88
2.17.2	Symmetry-adapted molecular orbitals	90
2.17.2.1	Representations	90
2.17.2.2	Symmetry elements, symmetry operations and point groups	91
2.17.2.3	Character tables	92
2.17.2.4	Projection operators	93
2.17.2.5	Reduction of a representation	95
2.17.3	Molecular orbitals for methane	96

2.18	Hückel molecular orbital theory	101
2.18.1	Ethene	101
2.18.2	Allyl radical	102
2.18.3	Benzene	104
2.18.4	π -Bond order	109
2.18.5	Free valence index	109
2.18.6	Charge distribution	110
2.19	Extended Hückel molecular orbital theory	111
2.20	Valence shell electron pair repulsion theory	113
2.21	Crystal-field and ligand-field theories	115
2.21.1	The hexacyanoferrate(II) ion	117
2.22	Paramagnetism	122
2.23	Apparently abnormal valence and three-centre bonding	124
2.23.1	Sulphur hexafluoride	124
2.23.2	Allyl anion	125
2.23.3	λ^5 -Borane	127
2.23.4	Shifting bonds	128
2.23.5	σ -Hole bonds	129
2.23.6	Diamondoid compounds	129
2.24	Theoretical techniques	130
2.25	Structural and physical characteristics of covalent solids	132
	References 2	134
	Problems 2	135
	Solution for Plotting exercise 2.1	143
	Solution for Plotting exercise 2.2	144
3	Molecular Compounds	146
3.1	Introduction	146
3.2	Electric moments and partial atomic charges	147
3.3	Polarization and polar molecules	149
3.3.1	The Langevin function	151
3.3.2	Electron polarization	156
3.3.2.1	Digression on electrical units	156
3.3.2.2	Polarization in gaseous species	156
3.3.3	Refractive index	158
3.3.4	Van der Waals equation of state	158
3.4	Polarization in condensed states	160
3.4.1	Ion-dipole interaction	160
3.4.2	Dipole-dipole interactions	161
3.4.2.1	Dipole-dipole interaction in a solid	161
3.4.2.2	Dipole-dipole interaction in a fluid	162
3.4.3	Induced dipole-induced dipole interaction	165
3.4.3.1	Vibrational bonding	169

3.4.4	Surface tension	169
3.4.4.1	Capillarity	170
3.5	Effect of frequency on polarization	171
3.6	Molar polarization	173
3.7	Static permittivity	175
3.7.1	Isotropic solids	177
3.8	Intermolecular potentials	179
3.9	Structure of liquids	182
3.9.1	Liquid–gas equilibrium	183
3.9.2	Radial distribution function	183
3.9.3	Diffraction studies on liquids	185
3.9.4	Internal energy of fluid	186
3.9.5	Simulation techniques	187
3.9.5.1	Monte Carlo	187
3.9.5.2	Molecular dynamics	188
3.10	Structural and physical characteristics of molecular solids	190
3.11	Hydrogen-bonded solids	191
3.11.1	Atomic force microscopy and hydrogen bonds	193
3.12	Classification of molecular solids	197
3.12.1	Inert gases	197
3.12.2	Groups 15, 16 and 17 elements	198
3.12.3	Small inorganic molecules	198
3.12.4	Clathrate compounds	200
3.12.5	Charge-transfer structures	201
3.12.6	π -Electron overlap compounds	202
3.12.7	Organic compounds	203
3.12.7.1	Classification system for organic compounds	206
References	3	210
Problems	3	211
4	Ionic Compounds	215
4.1	Introduction	215
4.2	Ionic bond	215
4.2.1	Crystal (cohesive) energy	217
4.3	Thermodynamic approach to crystal energy	217
4.3.1	Born–Fajans–Haber cycle	219
4.3.2	Sublimation enthalpy	220
4.3.3	Ionization energy	223
4.3.4	Dissociation enthalpy	223
4.3.5	Electron affinity	224
4.3.6	Enthalpy of formation	224
4.3.7	Precision of crystal energies	225
4.4	Electrostatic model for ionic crystals	225
4.4.1	Madelung constant	226
4.4.1.1	Series convergence	228

4.4.2	Crystal energy calculation	228
4.4.3	Polarization in ionic compounds	231
4.4.4	Crystal energy with polarization	231
4.5	Applications of crystal energies	232
4.5.1	Deducing electron affinities and related quantities	232
4.5.2	Compound stability	233
4.5.2.1	Energetics of inert gas compounds	233
4.5.2.2	Energetics of copper(I) fluoride and silver cyanide	234
4.5.2.3	Unfamiliar chlorides of sodium	235
4.5.3	Charges on polyatomic ions	235
4.6	Crystal chemistry	238
4.6.1	Ionic radii	240
4.6.2	Radius ratio and MX structure types	241
4.6.3	Radius ratio and MX_2 structure types	245
4.6.4	Structures of silicates	248
4.7	Structural and physical characteristics of ionic solids	251
4.8	Solubility of ionic compounds	252
4.8.1	Reference state for solubility	252
4.8.2	Solubility relationships	253
4.8.3	Solubility and energy	255
4.9	Spectra of ionic compounds	259
4.10	Heat capacity of ionic solids	260
4.11	Defects in ionic structures	261
4.11.1	Point defects	261
4.11.2	Defects of higher dimensions	264
4.11.3	Colour centres	265
4.11.3.1	F centres	265
4.11.3.2	H and V centres	266
4.11.4	Electrical properties in defect ionic structures	267
4.11.4.1	Fast-ion conductors	268
4.11.4.2	Doping	268
4.11.5	Image plates	269
References	4	270
Problems	4	272
5	Metallic Compounds	277
5.1	Introduction	277
5.2	Drude free-electron theory	277
5.3	Electrical conductivity	278
5.3.1	Drude–Lorentz model of metals	279
5.3.2	Ohm’s law	279
5.3.3	Mean free path	280
5.3.4	Hall effect	280
5.4	Thermal properties of metals	282
5.4.1	Classical solids	285

5.4.2	Einstein and Debye solids	286
5.4.3	Summary of classical free-electron theory	289
5.5	Wave-mechanical free-electron theory	291
5.5.1	Density of states	294
5.5.2	Fermi–Dirac distribution	295
5.5.2.1	Fermi energy and chemical potential	297
5.6	Band theory of metals	298
5.6.1	Wigner–Seitz cells and Brillouin zones	299
5.6.2	Energy bands and the Fermi level	301
5.6.3	Schrödinger equation in a periodic potential	302
5.6.4	Energy bands and electrical conduction	308
5.6.4.1	Hall effect revisited	309
5.7	Energy bands and molecular orbital theory	310
5.8	Semiconductors	313
5.8.1	Intrinsic semiconductors	314
5.8.2	Extrinsic semiconductors	315
5.8.3	p – n Junction semiconductors	315
5.8.4	Superconductors	316
5.9	Fuel cells, batteries and solar cells	318
5.9.1	Fuel cells	318
5.9.2	Batteries	319
5.9.3	Solar cells	322
5.9.3.1	Direct and indirect band gap semiconductors	323
5.10	Structures of metals	324
5.11	Structural and physical characteristics of metallic solids	326
5.12	Alloy systems	328
5.12.1	Copper–gold alloys	328
5.12.1.1	Order-disorder structures	329
5.12.2	Silver–cadmium alloys	330
5.13	Hume-Rothery rules for alloys	333
5.13.1	Intermetallic compounds	336
	References 5	337
	Problems 5	338
6	Nanoscience and Nanotechnology	342
6.1	Introduction	342
6.2	Physics of small systems	343
6.2.1	Quantum dots	344
6.2.1.1	Dimensionality and density of states function	346
6.2.1.2	Applications of quantum dots	347
6.2.2	Mechanical properties of nanocrystals	349
6.3	Carbon and its nanomaterials	351
6.3.1	Carbon black	351
6.3.2	Graphite	351

6.3.3	Fullerenes and buckyballs	353
6.3.4	Graphene	354
6.3.4.1	Chemical sensing	356
6.3.4.2	Graphene oxide	356
6.3.5	Carbon nanotubes and nanowires	356
6.3.6	After graphene	358
6.3.7	Graphite intercalation compounds	359
6.4	Magnetism in nanosize materials	361
6.4.1	Diamagnetic compounds	361
6.4.2	Paramagnetic compounds	362
6.4.3	Ferromagnetic, antiferromagnetic and ferrimagnetic compounds	362
6.5	Nanopolymers	365
6.6	Fabrication of nanosize materials	366
	References 6	369
	Problems 6	370
7	Computer-Aided Chemistry	373
7.1	Introduction	373
7.2	Plotting with Python	373
7.2.1	Plotting program (GRFN)	376
7.2.2	Contouring program (ANFN)	377
7.2.3	Angular functions field figures (PLOT)	377
7.3	Hückel molecular orbitals (HUCK)	379
7.3.1	Hückel extension: h and k parameters	380
7.4	Linear least squares (LSLI)	380
7.4.1	Transmission of errors	381
7.5	Madelung constants (MADC)	381
7.6	Matrix operations (MATS)	382
7.7	Radial wavefunctions (RADL)	382
7.8	Angular wavefunctions ('Orbitron')	382
7.9	Gaussian quadrature (QUAD)	382
7.10	Roots of polynomials (ROOT)	383
7.11	Inverse r^6 and r^{12} curves (LJON)	383
7.12	Electron-in-a-box (BOXS)	383
7.13	Waveforms (WAVE)	384
	References 7	384
	Problems 7	384
Appendices		
A1	Stereoviewing and Stereoviewers	387
	References A1	387

A2 Miller Indices	389
Exercise A1	391
References A2	391
A3 Bragg Reflection of X-rays from Crystals	392
Exercise A2	394
Reference A3	394
A4 Boltzmann Distribution from the Hypsometric Formula	395
Reference A4	396
A5 Mean Classical Thermal Energy and the Equipartition Theorem	397
A5.1 Mean kinetic energy	397
A5.2 Equipartition theorem	398
A6 Spherical Polar Coordinates	399
A6.1 Coordinates	399
A6.2 Volume element	400
Exercise A3	400
A7 Gamma Function $\Gamma(n)$	401
References A7	402
A8 Reduced Mass	403
A9 Solution of a Differential Equation	405
A10 Determinant Expansion, Matrices and Matrix Properties and Hückel Molecular-Orbital Coefficients	407
A10.1 Expansion of a determinant	407
A10.2 Matrices	408
A10.2.1 General matrix	408
A10.2.2 Row matrix	408
A10.2.3 Column matrix	408
A10.2.4 Symmetric, skew-symmetric, equal and identity matrices	408
A10.2.5 Addition and subtraction of matrices	409
A10.2.6 Transposition	409
A10.2.7 Multiplication with matrices	409
A10.2.8 Multiplicative properties of matrices	410
A10.2.9 Inverse of a matrix	410
A10.2.10 Orthogonal and unitary matrices	411
A10.2.11 Matrices, rows and columns	412
A10.3 Hückel molecular orbital wavefunction coefficients	412
A11 Electrostatics and Volume of Molecules in a Gas	414
A11.1 Law of force	414

A11.2 Coulomb's law	414
Exercise A4	415
A11.3 Permittivity	415
A11.3.1 Measurement of relative permittivity	415
A11.4 Potential and field of a charge	416
Exercise A5	418
A11.5 Potential of an ideal dipole	418
A11.6 Capacitance	420
A11.7 Clausius–Mosotti and Lorentz–Lorenz equations	421
A11.8 Volume of molecules in a gas	425
A12 Configurational Energy	426
Reference A12	427
A13 Numerical Integration	428
A13.1 Introduction	428
A13.2 Numerical methods	429
A13.2.1 Simpson's rule	429
A13.2.2 Gaussian quadrature	429
References A13	430
A14 X-ray Crystallographic Structure Analyses of Potassium Chloride and Sodium Chloride	431
References A14	434
A15 Calculation of Madelung Constants	435
References A15	436
A16 Equation of State for a Solid	437
References A16	438
A17 Partial Molar Quantities and Standard States	439
A17.1 Introduction	439
A17.2 Partial molar volume	439
A17.3 Partial molar entropy	440
A17.3.1 Measurement of the partial molar entropy of a hydrated ion	440
A17.4 Generalized description of partial molar quantities	441
A17.5 Partial molar enthalpy	442
A17.6 Standard states and reference states	443
References A17	446
A18 Debye Limiting Law	447
References A18	449

A19 Quantum Statistics	450
A19.1 Introduction	450
A19.2 Fermi–Dirac distribution	450
A19.3 Lagrange undetermined multipliers	453
References A19	456
A20 Reciprocal Space and Reciprocal Lattice	457
A20.1 Reciprocal space	457
A20.2 Reciprocal lattice and Ewald’s construction	460
Exercise A6	462
References A20	462
A21 Wave Packets	463
A21.1 Particle and wave	463
A21.2 Localized particle: superposition of waves	463
A21.3 Phase and group velocities	465
A21.4 Localized particle	466
Exercise A7	469
Answers to Exercises	470
Tutorial Solutions	
Introductory note	471
Solutions 1	471
Solutions 2	473
Solutions 3	489
Solutions 4	493
Solutions 5	500
Solutions 6	505
Solutions 7	509
References	513
Index	515