Contents
Notes On General Chemistry, 2e

Chapter 1, The stuff of chemistry 1
- Avogadro's hypothesis 2
- Incomplete combustion of acetylene 3
- Building blocks of atoms 3
  - Charge-to-mass ratio of the electron 3
  - Charge, and so mass of the electron 4
  - The nucleus 4
  - Protons, neutrons, and isotopes 6
- Relative atomic mass 6
- Absolute atomic mass 7
- Calculating chemical amounts 8
  - Given mass of an element, how many atoms do we have 8
  - Given mass of a compound, how many molecules do we have? 9
  - Given mass of a compound, how many atoms do we have? 9
  - How much mass is needed to have a given number of molecules? 10
  - How much mass is needed to have a given number of atoms? 10
- Problems illustrating calculations with moles 10
  - Using density to count atoms 10
  - Mass percentage in chemical synthesis 11
  - Mass percentage in a compound 12
- Calculating chemical amounts in chemical reactions 12
  - Writing balanced chemical equations 13
  - Percentage yield 14
- Limiting reagent 14
  - Limiting reagent in sandwich making 15
  - What we need versus what we have 15
  - Limiting reagent in iron thiocyanate formation 16
  - Limiting reagent in combustion of hydrogen 16
- Study problem on limiting reagent and percentage yield 17
- Composition of solutions 18
  - Making a solution of known molarity 19
  - Diluting a solution of known molarity 19
  - Molarity and titration 19

Stoichiometry of reactions in solution 20

Chapter 2, Quantum aspects of light and matter 21
- Properties of waves 21
  - A review of sines and cosines: SOH-CAH-TOA 22
  - Representing wave properties mathematically 24
  - The speed of a wave: phase velocity 25
  - Calculations with waves 26
  - Angular frequency and angular wavenumber. 27
- Interaction of light with matter: resonant "tugs" 27
- Energy conservation in interaction between light and matter 28
- Amount of energy exchanged between light and matter 29
- Photoelectric effect and photoionization 31
- Particles of light 33
  - Measuring the momentum of light: Compton scattering 36
- Waves of matter 38
- Electron in a box 39
  - Absorption spectrum of an electron in a box 40
  - Energy balance in the spectra of an electron in a box 41
- Taking stock 41
- What's waving in a matter wave? 42
- Born interpretation: What's waving is *probability amplitude* 43
  - Calculating probability densities 45
  - Are wavefunctions real? 47
- How does light make electrons jiggle? 47
  - Example: Electron in a one-dimensional box 48
  - Example: Electron in hydrogen atom 49
- Representing a "particle" with waves: wavepackets 50
  - Wavepacket example 51
  - Heisenberg uncertainty principle 53

Chapter 3.1, Atomic wavefunction family album 55
- Spherical (s) family 56
- Dumbbell (p) family 57
- Cloverleaf (d) family 58
- Questions 59

Chapter 3.2, Atlas of electrons in atoms 61
- How we label wavefunctions of electrons in atoms 61
- Dissecting wavefunctions of electrons in atoms 61
- Caution: Spherical polar representations can be misleading! 64
- Constructing wavefunctions of electrons in atoms 68
- Shell amplitude, shell density, and probability density 70
  - 4s 73
  - $4p_x$ 74
  - $4d_{x^2-y^2}$ 76

Chapter 3.3, Energies of electrons in atoms 77
- Atomic first ionization energies 77
- Atomic electron configurations 77
- Electron shielding 79
  - Shielding reflects wavefunctions details near the nucleus 79

Estimating shielding: Effective nulcear charge 81
Shielding in excited states 82
Li atom Rydberg series 82
Na atom Rydberg series 83

Chapter 3.4, Why atoms don't collapse 85
Balance of kinetic and potential energy 85
Problems 86
Hydrogen atom energy balance 86
Problems 87
Helium ion energy balance 88
Problems 89

Chapter 3.5, Many-electron atoms: Fermi holes and Fermi heaps 91
The orbital approximation 91
Electrical shielding 92
Electrical repulsion 92
Two electrons 92
Three electrons 93
The Pauli principle 93
Electron intrinsic magnetic moment 94
Indistinguishability of electrons 94
Electronic configurations in atoms 95
Hydrogen 95
Helium 95
Lithium 96
Pauli exclusion principle 97
Relative stability of 1s2p configurations—Fermi holes and Fermi heaps 98
Visualization of 1s2p Fermi holes and Fermi heaps 99
Relative stability of $2p^2$ configurations 100
Configurations 100
Relative energies 102
Fermi hole and Fermi heap 102
Visualization of 2p2p Fermi holes and Fermi heaps 103

Chapter 4.1, Quantum picture of molecules 105
Using Coulomb's law to analyze ionic and covalent bonding 105
Electronegativity and ionic character 105
Different definitions of electronegativity 107
Coulomb's law 107
Ionic bonds 108
Covalent bonds 108
Ionic character 109
Lewis model of chemical bonding 109
Rules for constructing Lewis structures 110
Formal charge 110
Odd-number of electrons 110
Octet-deficient structures 111
Valence-shell expansion 111
VSEPR model of molecular shape 111
Polar nature of water 112

Electrolytes 112
Molecular shape and dipole moments 113
Quantum mechanics of the covalent bond 113
Molecular orbitals 117
Flow of electron density in bonding and antibonding MO's 118
Bonding in homonuclear diatomic molecules 119
Bonding in heteronulcear diatomic molecules 120
What makes polyatomic molecules rigid 121

Chapter 4.2, Bonding, antibonding, and nonbonding molecular orbitals 123
Effect on energy of orbital overlap in molecular orbitals 123
Probability density changes in molecular orbitals 125
1sσ density change 126
2sσ density change 128
2 p_z σ density change 129
2 p_x π density change 130
2 p_x 2 p_z density change 131

Chapter 4.3, Hybrid atomic orbitals 133
Atomic wavefunctions 133
sp hybrid atomic orbitals 135
sp^2 hybrid atomic orbitals 138
sp^3 hybrid atomic orbitals 139

Chapter 5, Properties of gases 141
Physical properties of gases 141
Units of pressure 141
Demonstrating the force of the atmosphere 143
Is atmospheric pressure a big deal? 1 atm = 6 Dans! 143
Experiencing pressure 143
Interdependence of P, V, T and n 144
Effect of temperature on pressure 144
Effect of temperature on volume 145
Effect of amount on volume 145
Effect of pressure on volume 146
Ideal gas law 146
Recipe for gas law problems 147
Additional problems 148
Gas mixtures: Dalton's law of partial pressure 149
Using partial pressure to monitor reaction progress 150
Kinetic molecular theory 151
The meaning of temperature 153
Understanding the ideal gas law in terms of particle motion 154
Distribution of speeds in a gas 155
Example speed distribution 155
Maxwell-Boltzmann speed distribution 157
What are the units of $F(u)$? 157
How is $F(u)$ evaluated? 158
What is the general form of $F(u)$? 159
Real gases 159

Van der Waals equation 160
Ideal-gas limit 161
Using the van der Waals equation 162
Compressibility ratio, *z*: a tool to monitor deviations from ideality 163
Potential energy curve 163
Very low pressure 165
Moderate pressure 165
High pressure 165
Effect of temperature 165
Compressibility ratio, *z*, for van der Waals gases 166
When do we need the van der Waals equation? Virial expansion 168
Ideal gases, van der Waals gases, and real gases 172

Chapter 6, Condensed phases 173
Vapor pressure 173
Phase diagrams 173
Water to steam without boiling! 174
Evaporation of water 174
Composition of solutions 175
Example: Oxtoby and Nachtrieb, 3e, problem 4-24 175
Making a solution of known molarity 176
Diluting a solution of known molarity 176
Molarity and titration 177
Stoichiometry of reactions in solution 177
Colligative properties 178
Vapor-pressure lowering 178
Example: Oxtoby and Nachtrieb, 3e, problem 4-44 178
Boiling-point elevation 179
Example: Oxtoby and Nachtrieb, 3e, problem 4-46 179
Freezing-point depression 179
Demonstration 180
Example 180
Osmotic pressure 180
Example: Oxtoby and Nachtrieb, 3e, problem 4-56 181
Example: Predicting osmotic pressure 181
Volatile solutes: Henry's law 182
Example: Oxtoby and Nachtrieb, 3e, problem 4-60 182

Chapter 7, Chemical equilibrium 185
How chemical equilibrium comes about 185
Law of mass action 186
Equilibrium constant 186
Equilibrium expressions in terms of pressures or concentrations 187
Equilibrium expression examples 188
K depends on how the equilibrium is written 189
K for combined reactions 190
Using pressure to evaluate *K* 190
Fixed K does not mean fixed ratios of partial pressures 191
Direction of change 192
Using *K* to evaluate equilibrium pressures 194

Approximation technique: Neglect x when it is "small" 194
Approximation technique: Arrange conditions so x is "small" 196
Approximation technique: Successive approximations 198
Response to disruption of equilibrium 199
Partial pressure change 199
Volume change 200
Numerical example 201
Le Chatelier's principle 202
Changing amounts 202
Changing volume (and so pressure) 203
Changing temperature 203

Chapter 8, Acid-base equilibria 205

Road map of acid-base equilibria 205
Acid-base reactions 206
Acid ionization constant K_a 206
Base ionization constant K_b 206
Water autoionization constant K_w 207
pH 208
Origin of the notation pH 209
Regime 1: pure strong acid (or base) 210
Regime 1: pure weak acid (or base) 211
Pure weak acid example 212
Pure weak base example 213
Regime 3: Neutralized weak acid (or base): hydrolysis 214
When hydrolysis is important: Weak can be strong! 215
Regime 2: Partially neutralized weak acid (or base): buffer 216
Calculation of buffer action 217
Adding strong acid to a weak-acid buffer 217
Step 1: Limiting-reagent stoichiometry 218
Step 2: Re-equilibration 218
Adding strong base to a weak-acid buffer 218
Step 1: Limiting-reagent stoichiometry 219
Step 2: Re-equilibration 219
Comparison to unbuffered solution 219
Henderson-Hasselbalch equation 219
Regime 4: Excess base (or acid) 220
Practice with regimes 221
Putting it all together: titration 222
Strong acid/strong base titration 222
Regime 1: pH of pure acid 223
Regime 2: pH of partially neutralized acid 223
Regime 3: pH of exactly neutralized acid 223
Regime 4: pH of excess base 223
Calculation of titration curve 224
Weak acid/strong base titration 225
Equivalence volume 225
Pure weak acid 226
Partial neutralization of weak acid by strong base 226

Exact neutralization of weak acid by strong base 226
Excess strong base 227
Calculation of pH 227
Results 228
Strong acid–strong base versus weak acid–strong base titration 228
Limiting-reagent calculations in titrations: Study problems 229
Add strong base to a weak acid to give a particular pH 229
Add strong acid to a weak-acid salt to give a particular pH 230
Titration recipes 231
Polyprotic acids 231

Chapter 9, Precipitation equilibria 235
Introduction 235
Calculating solubility from K_{sp} 235
Precipitation 236
Diluted concentrations 236
Will precipitation occur? 237
Calculating the precipitation 237
Effect of common ions on solubility 238
Common-ion effect example 238
Effect of pH on solubility 239
Contribution to pH by water autoionization and by insoluble hydroxides 239
Effect of buffered pH on solubility of insoluble hydroxides 240
Salts of weak acids (and of weak bases) 241

Chapter 10, Energy balance: First law of thermodynamics 243
Overview 243
Forest for the trees 243
Language of thermodynamics 244
Energy: Work and heat 245
Pressure-volume work 245
Heat 246
Equivalence of heat and work 247
Temperature leveling 248
Heat capacities of the ideal gas 249
Constant volume heat capacity, c_V 249
Constant pressure heat capacity, c_P 250
Heat capacities of real gases 251
First law of thermodynamics 252
Example thermodynamic transformations of an ideal gas 253
Heating 253
Isothermal compression 1 254
Isothermal compression 2 254
Enthalpy 255
Relation between ΔE and ΔH for physical transformations of a gas 256
Study problem 258
Enthalpy changes in chemical reactions 258
The so-called high-energy phosphate bond 259
Enthalpy change in chemical reactions: Hess's law 259
Relation between ΔE and ΔH for chemical reactions 261

Enthalpy change of formation 262
Estimating reaction enthalpies from average bond enthalpies 264
Effect of temperature enthalpy changes 265
Study problem 267
Getting thermodynamic data 267

Chapter 11.1, Spontaneity: Second law of thermodynamics 269

Introduction 269
- Chemical equilibrium 269
- Reaction quotient and equilibrium constant 270
- Roadmap 270
- Forest for the trees 271

Approach to reversible transformation 271
- Isothermal transformation of an ideal gas 271
- Work is least and heat is greatest for reversible transformation 276
- Energy source for ideal gas expansion 277
- Energy dispersal is why a gas can extract heat from its surroundings 279

Thermodynamic view: Entropy and the second law 280

Computing entropy change 282
- Direction of heat flow 282
- Melting of ice 283
  - System entropy change 284
  - Surroundings entropy change 285
  - Total entropy change 286
  - Melting of ice at 0°C 286
  - Melting of ice at -10°C 286
- Master rule of entropy change calculations 286
- Isothermal free expansion of an ideal gas 287
- Non-isothermal ideal gas processes 287
  - Step 1 288
  - Step 2 289
  - Checking that entropy change is independent of path 289
- Entropy changes in cyclic transformations! 290
- Flash evaporation of water 291
- When to use $T_2 - T_1$; when to use $\ln(T_2 / T_2)$ 292
- When the temperature of the surroundings changes 292
  - Study problem 293
  - A generalization 293

Microscopic entropy changes: Boltzmann's approach 293
- Converting probabilities to scientific notation 295
- Counting microstates: Binomial coefficient 296
- Calculating entropy for a model universe 297

The third law of thermodynamis: Standard-state entropies 299

System-only measure of spontaneity: Gibbs free energy 300

Computing free energy change 301
- Isothermal expansion of an ideal gas 301
- Using free energy change to estimate the temperature of a phase change 302
- Example of spontaneity driven by entropy increase in the surroundings 303
- Using temperature to make a process spontaneous 304

- Connection between Gibbs free energy and equilibrium 304
- Units of ΔG for chemical transformations 307
- "Distance" from equilibrium 307
  - Temperature dependence of equilibrium: van't Hoff equation 309
  - Le Chatelier's principle and temperature dependence 310
  - Temperature and vapor pressure: Clausius-Clapeyron equation 311

Chapter 11.2, Counting distinguishable arrangements 313
  - Molecules distributed in space 313
    - Questions 314
  - Energy distributed among molecules 314
    - Questions 316
  - ACS *Chemistry*, 8.14 Consider This: Temperature and entropy change 316
    - Questions 318
  - Stirling's approximation for $n!$ when n is very large 318
    - Derivation of Stirling's approximation 319

Chapter 12, Electrochemistry: Harnessed spontaneity 321
  - Oxidation numbers 321
    - Heuristic determination of oxidation state 322
    - Oxidation number change and types of inorganic reactions 322
  - Balancing redox equations 323
    - Big piece one: Get the balanced half-reactions for acidic solution 323
    - Big piece two: Combine the half-reactions into the full equation 324
    - Big piece three: If necessary, convert the equation to basic solution 325
    - Disproportionation 325
    - Using oxidation numbers as a guide 325
  - Harnessing electron flow in redox processes 326
  - The Nernst equation 327
  - Quantifying electrochemical cells 329
  - Where the Nernst equation comes from 330
  - Effect of concentration on voltage 331
  - The Nernst equation and equilibrium 331
  - Standard reduction potentials 333
    - Calculating standard reduction potentials 335
    - Strength of reducing and oxidizing agents 335
  - How to combine half-cell potentials (use ΔG!) 336
  - Reduction potential diagrams 337
  - Cell potentials and equilibrium constants for non-redox processes 338
  - Concentration cells 339
  - Predicting the effect of concentration on cell potentials 340
  - Effect of pH and pressure on cell voltage 340
  - Study problems: Effect of pH on reduction potentials 341

Chapter 13, Kinetics: Approach to equilibrium 343
- Overview of kinetics 343
- Rate versus concentration: differential rate laws 344
  - Rate is different from rate of change in concentration 344
  - Determining rate versus concentration 345
  - Finding reaction orders 347
  - Study problem: Determining reaction orders algebraically 348

Concentration versus time: integrated rate laws 349
- Zeroth-order integrated rate law 349
- First-order integrated rate law 350
- Second-order integrated rate law 352
- Using concentration versus time to determine reaction order 353
- Half-life 356
  - Zumdahl, *Chemical Principles*, 2e, exercise 15-23 356
  - Zumdahl, exercise 15-23, changed to second order 357
  - Comparison of first- and second-order decay 358
- Half life simulation using coin flips 359
  - Simulated results 359
  - Idealized decay curve 360
  - Counting class attendance by counting half lives 360
  - Estimating how many half lives have elapsed 360

Mechanisms and rate 361
- First step slowest 361
- Intermediate step slowest 361

Connection between rate and equilibrium 362

Effect of temperature on rate constants 363
- Origin of the exponential temperature dependence 365
- Determining activation energy and Arrhenius factor 366
- An example: Effect of temperature on iodine clock reaction 368
- Challenge problem 368

Effect of temperature on equilibrium constants 369
- Thermodynamic analysis 369
- Kinetic (detailed balance) analysis 369

Connection between rates and thermodynamics 373
- Enthalpy change and activation energies 373
- Entropy change and pre-exponential factors 374

Appendix 1, Significant figures in numerical calculations 377
- Significant figures involving multiplication and division 377
- Significant figures involving addition and subtraction 378
- Rounding 378
- Significant figures involving logarithms 378

Appendix 2, Approximating with logarithms 381
- Definition of logarithm 381
- Approximating numerical values of logarithms 381
- Calculating natural logarithms 383
- Evaluating powers of ten (base 10 antilogarithms) 383
- Evaluating powers of e (base e antilogarithms) 384
- Using logarithms to evaluate powers and roots 384
- Significant figures involving logarithms 385

Appendix 3, Rises and runs, slopes and sums: tools from calculus 387

Slopes 387
- Linear variation, $f(x) = a\,x$ 388
- Quadratic variation, $f(x) = a\,x^2$ 388
- General variation, $f(x) = a\,x^n$ 389

Inverse linear variation, $f(x) = a\,x^{-1}$ 389
Inverse quadratic variation, $f(x) = a\,x^{-2}$ 390
General variation, $f(x) = a\,x^{-n}$ 391
Trigonometric variation, $f(x) = \sin(a\,x)$ 391
Trigonometric variation, $f(x) = \cos(a\,x)$ 392
Sums 393
A remarkable special case: $f(x) = \ln(x)$ 394
Logarithmic properties of $\int_1^x (1/x)\,dx$ 395
Base of the natural logarithm: e 395
Logarithmic properties of the natural logarithm 396
Natural logarithm of a product 397
Natural logarithm of a reciprocal 397
Postscript 398
Summary 398
Appendix 4, Guide to *Mathematica* 399