## CONTENTS

Preface ..... xxv
How to use the workbooks, exercises, and problems ..... xxxi
Chapter 1 Temperature, pressure, molar volume, and equilibrium ..... 1
Introduction ..... 1
System and environment ..... 1
Temperature and thermal equilibrium ..... 2
Thermometer ..... 2
Temperature scales ..... 3
Pressure and mechanical equilibrium ..... 7
Calculating the pressure in a cylinder ..... 8
The units of pressure ..... 8
The units Torr, atm, bar, and psi ..... 9
Conversion between units ..... 10
Volume, density, and molar volume ..... 11
Intensive and extensive quantities ..... 12
Equilibrium ..... 13
Equilibrium and environment ..... 13
Supplement 1.1 An excerpt from Fahrenheit's article ..... 14
Supplement 1.2 Origin of the pressure units atmosphere and Torr ..... 16
Problems ..... 19
Chapter 2 The equation of state ..... 21
Introduction ..... 21
The state of a gas or a liquid at equilibrium ..... 21
The equation of state ..... 22
Solids are different ..... 22
The ideal gas equation ..... 24
Units ..... 24
When and why the ideal gas law is valid ..... 26
The van der Waals equation of state ..... 28
Accurate equations of state ..... 29
Summary and perspective ..... 30
Problems ..... 31
Chapter 3 How to use the equation of state ..... 33
Calculate pressure when you know molar volume and temperature ..... 33
Why we calculate pressure ..... 33
How to calculate pressure ..... 34
Calculate molar volume when you know pressure and temperature ..... 36
Why we calculate the molar volume ..... 36
An example of molar volume calculation ..... 38
Calculate temperature when you know molar volume and pressure ..... 40
When such calculations are needed ..... 40
Summary of Chapters 1-3 ..... 40
Problems ..... 41
Supplement 3.1 How to get your own equation of state ..... 45
Least squares fitting ..... 50
Why we use the square of the error ..... 50
Minimizing the global error ..... 51
Determining the parameters in the van der Waals equation ..... 53
Problems ..... 56
Chapter 4 Thermodynamic transformations ..... 59
Definition and examples of thermodynamic transformations ..... 59
Non-equilibrium transformations ..... 61
Initial and final states ..... 61
The path of the transformation ..... 62
Equilibrium transformations ..... 62
Why we study equilibrium transformations ..... 64
Supplement 4.1. More about equilibrium transformations and their paths ..... 65
Two equilibrium transformations with the same initial and final state but different paths ..... 65
Chapter 5 Work ..... 69
Introduction ..... 69
The definition of work ..... 70
The sign convention ..... 71
Units ..... 71
Work is an extensive quantity ..... 72
No change in volume, no work ..... 72
Work is performed against an opposing force ..... 73
There are many ways of exchanging work ..... 73
How to calculate the work in a finite transformation ..... 73
The work performed in a finite transformation ..... 73
Work performed in an isothermal transformation ..... 76
What an isothermal transformation is ..... 76
The work performed in an isothermal expansion ..... 77
A numerical calculation of isothermal work ..... 78
The work performed in an isobaric transformation ..... 81
What an isobaric transformation is ..... 81
A numerical calculation of the work performed in an isobaric transformation ..... 81
The work performed in a transformation depends on the path ..... 83
Work is not a function of state ..... 86
Problems ..... 87
Chapter 6 Heat ..... 91
What is heat? ..... 91
The caloric theory ..... 91
What is transferred from a hot body to a cold one ..... 93
How to measure the amount of heat ..... 94
Heat and work are equivalent ..... 94
The amount of heat has a sign ..... 95
Thermal coefficients: definitions ..... 95
Heat exchanged at constant pressure ..... 96
Heat exchanged at constant volume ..... 97
The heat exchanged when pressure changes and temperature is constant ..... 97
The heat exchanged in a general transformation ..... 98
Information regarding the thermal coefficients ..... 99
Heat capacity at constant pressure ..... 99
The temperature dependence of $C_{p}$ ..... 101
The pressure dependence of $C_{p}$ ..... 103
Heat capacity at constant volume ..... 104
Calculations of the heat exchanged in simple transformations ..... 106
The heat transferred when a system is heated at constant volume ..... 108
Heat exchange when two bodies of different temperatures are brought into contact ..... 109
The number of moles ..... 111
Problems ..... 114
Supplement 6.1. Heat is a form of motion: an experiment in boring cannon ..... 115
Supplement 6.2. Joseph Black, heat capacity ..... 122
Supplement 6.3. A more extensive look at heat theory and calculations ..... 127
Information regarding $\ell_{p}$ and $\ell_{v}$ ..... 129
$\ell_{p}$ and $\ell_{v}$ for an ideal gas ..... 130
The heat exchanged in an infinitesimal transformation ..... 131
The heat exchanged in a finite transformation ..... 131
The heat exchanged in an isothermal compression: general equation ..... 132
The heat exchanged in an isothermal compression of an ideal gas ..... 133
The heat exchanged in an isothermal compression of a van der Waals gas ..... 134
The case of a real gas: implementation ..... 137
A numerical evaluation of $q_{T}$ ..... 138
Problems ..... 140
Chapter 7 Reversible and irreversible transformations ..... 143
Introduction ..... 143
Definition ..... 144
Heat transfer ..... 144
Diffusion ..... 145
An equilibrium transformation is reversible ..... 146
Chapter 8 Path-dependent and path-independent quantities ..... 149
Path-independent line integrals ..... 149
Line integrals in thermodynamics ..... 149
Most line integrals depend on the path (the line) ..... 153
Path-independent integrals: an example ..... 154
Exact differentials ..... 156
Path-independent line integrals: theorems ..... 157
Applications to thermodynamics ..... 161
Work and heat depend on path ..... 161
A proof that $\int \delta W$ depends on path ..... 162
Exact differentials and functions of state ..... 163
Chapter 9 First and second laws of thermodynamics ..... 165
The formulation of the laws ..... 165
Introduction ..... 165
The First Law ..... 165
The Second Law ..... 166
The Third Law ..... 166
Common features of energy and entropy ..... 167
$\int d U$ and $\int d S$ are path-independent ..... 167
$U$ and $S$ are functions of state ..... 168
Maxwell relations ..... 168
Adding a constant to entropy or energy causes no measurable change ..... 169
$U$ and $S$ are extensive properties ..... 170
A few comments about the First Law ..... 170
Energy conservation ..... 170
The First Law today ..... 174
A few comments about the Second Law ..... 175
The direction of a transformation ..... 175
Impossible processes ..... 177
Why this is useful ..... 177
Chapter 10 Helmholtz and Gibbs free energies ..... 179
Introduction ..... 179
Why do we need other functions besides entropy? ..... 179
A convenient form for the First and Second Laws ..... 179
Second Law for a transformation keeping $U$ and $V$ constant ..... 180
Helmholtz free energy $A$ ..... 182
Second Law in terms of changes in $V$ and $T$ ..... 182
Transformations at constant T and V ..... 183
Using A: a hint ..... 184
Gibbs free energy $G$ ..... 184
The definition of Gibbs free energy ..... 184
Some properties of Gibbs free energy ..... 185
The change of $G$ in a transformation in which $T$ and $p$ are held constant ..... 185
Using Gibbs free energy: a hint ..... 186
Chapter 11 How to calculate the change of entropy in an equilibrium transformation ..... 187
Introduction ..... 187
Which variable to use ..... 187
The variables $T$ and $p$ : theory ..... 188
The change ds of entropy when pressure changes by $d p$ and temperature by $d T$ ..... 189
Notation for partial derivatives ..... 189
Maxwell's method ..... 191
The derivative $(\partial s / \partial p)_{T}$ ..... 191
The derivative $(\partial s / \partial T)_{p}$ ..... 192
Combine these results to get an expression for $d s$ ..... 193
The change of entropy in a transformation in which $T$ and $p$ change by a finite amount ..... 193
The variables $T$ and $v$ : theory ..... 193
The calculation of $(\partial s / \partial v)_{T}$ ..... 194
The change in entropy when both $T$ and $v$ change ..... 195
The change in entropy in a finite transformation ..... 195
Calculations of entropy change in various transformations ..... 196
Entropy change in an isobaric transformation ..... 196
The change of entropy in an isothermal transformation ..... 198
The change of entropy in a general transformation ..... 202
The change of entropy: numerical results ..... 204
How to use the tables of data to calculate entropy changes ..... 204
Problems ..... 205
Supplement 11.1. Using Maxwell's method to derive useful equations ..... 208
Using Maxwell equations ..... 208
Supplement 11.2. Obtaining new equations by changing variables ..... 211
An equation for $(\partial v / \partial T)_{p}$ ..... 212
A more general method for calculating $(\partial v / \partial T)_{p}$ ..... 213
An equation for $C_{p}-C_{v}$ ..... 214
Supplement 11.3. Adiabatic transformations ..... 215
The transformation path in an adiabatic transformation ..... 216
The equation for the final temperature ..... 217
An example of adiabatic compression ..... 218
Chapter 12 Enthalpy and energy change during a thermodynamic transformation ..... 219
Introduction ..... 219
Heat and enthalpy ..... 221
The connection between the enthalpy change and heat ..... 222
Heat and energy ..... 222
How to calculate the enthalpy change in a transformation:223
The change of enthalpy in an infinitesimal transformation ..... 223
The change of enthalpy in a finite transformation ..... 225
Choosing a path ..... 225
How to calculate the enthalpy change in a transformation: an example ..... 227
The change of enthalpy $\Delta h_{A}$ when $T$ changes and $p$ is constant (path A) ..... 228
The change of enthalpy $\Delta h_{B}$ when pressure changes and temperature is held constant ..... 229
The first difficulty ..... 229
The second difficulty ..... 231
The final result for $\Delta h_{B}$ ..... 233
An example of a calculation of $\Delta h_{B}$ ..... 234
The order of magnitude of $\Delta h_{B}$ ..... 234
The use of tables to calculate enthalpy changes with temperature ..... 235
Supplement 12.1. Energy changes in a thermodynamic transformation ..... 238
The change of energy in an infinitesimal transformation in which $T$ and $v$ are changed ..... 238
The change of energy in a finite transformation in which $T$ and $v$ are changed ..... 238
Another way of calculating energy changes ..... 239
Supplement 12.2. Isenthalpic transformations ..... 240
This transformation takes place without a change of enthalpy ..... 241
The change of temperature caused by an isenthalpic transformation ..... 242
Isenthalpic transformations are used for cooling ..... 243
Ideal gas ..... 246
Chapter 13 Thermochemistry ..... 247
Introduction ..... 247
Definition of the heat of reaction ..... 248
Two reactions used as examples ..... 248
The definition of the heat of reaction ..... 249
The initial state ..... 249
The final state ..... 249
Sign convention ..... 250
The presentation of data: standard state ..... 250
The connection between the heat of reaction and the enthalpy of the participants ..... 251
Enthalpy change in a reaction ..... 252
The dependence of the heat of reaction on temperature and pressure ..... 255
Enthalpy change in a transformation from $\sigma_{i}$ to $\sigma_{f}$ ..... 255
The heat of reaction at $T_{f}$ and $p_{f}$ ..... 256
The change of the heat of reaction with temperature ..... 257
The change of heat of reaction with pressure ..... 257
An example: the heat of reaction for ammonia synthesis ..... 258
The heat of reaction $\Delta H$ ..... 259
The temperature dependence of the heat of reaction ..... 260
The heat of reaction at 623.15 K and 394.8 atm ..... 262
Calculating the heat of a reaction from heats of formation or combustion ..... 264
Heats of formation: definition ..... 266
The connection between the heat of reaction and the heats of formation of the compounds ..... 266
Where to get heats of formation ..... 269
The use of heats of combustion to calculate heats of reaction ..... 270
Supplement 13.1. Calculating the heat of one reaction from the heats of other reactions ..... 274
Problems ..... 281
Chapter 14 The change of chemical potential during an equilibrium transformation ..... 285
Introduction ..... 285
The change of chemical potential calculated with Eq. 14.4 ..... 286
How to evaluate $\Delta \mu_{1} \equiv \mu\left(T_{f}, p_{i}\right)-\mu\left(T_{i}, p_{i}\right)$ ..... 287
An example of evaluation of $\Delta \mu_{1} \equiv \mu\left(T_{f}, p_{i}\right)-$ $\mu\left(T_{i}, p_{i}\right)$ ..... 288
How to evaluate $\Delta \mu_{2} \equiv \mu\left(T_{f}, p_{f}\right)-\mu\left(T_{f}, p_{i}\right)$ ..... 289
Calculating $\Delta \mu=\mu(130 \mathrm{~K}, 600 \mathrm{~atm})$ $-\mu(298.15 \mathrm{~K}, 1 \mathrm{~atm})$ ..... 293
Additional material about chemical potential ..... 295
The pressure dependence of the chemical potential of an ideal gas ..... 295
Fugacity ..... 295
The dependence of chemical potential on temperature ..... 296
Calculating $\mu$ from $\mu=h-T s$ ..... 297
Problems ..... 298
Chapter 15 The chemical potential of a compound in a mixture ..... 301
General remarks ..... 301
Infinitesimal transformations ..... 302
The chemical potential of a compound in a mixture ..... 303
The change of Gibbs free energy when I change temperature, pressure, and composition ..... 303
Change of variables ..... 304
The chemical potential of ideal mixtures ..... 307
The partial pressure of a gas in an ideal mixture ..... 307
The chemical potential of a gas in an ideal mixture ..... 308
A few words about Josiah Willard Gibbs ..... 309
Chapter 16 Mixtures: partial molar quantities and activities ..... 311
Partial molar quantities ..... 311
The correct formula ..... 314
Partial molar volume is an intensive quantity ..... 316
Other partial molar quantities ..... 317
Partial molar enthalpy and the heat of mixing ..... 318
Chemical potential as a partial molar quantity: the Gibbs-Duhem equation ..... 319
Equations similar to the Gibbs-Duhem equation for other partial molar quantities ..... 321
How to determine partial molar quantities from measurements ..... 322
Relations among partial molar quantities ..... 325
The composition dependence of chemical potential: ideal solutions ..... 327
The definition of an ideal solution ..... 327
The change of volume when we mix compounds to form an ideal solution ..... 327
The enthalpy of an ideal mixture ..... 328
The heat of mixing to form an ideal solution ..... 329
The entropy of mixing to form an ideal solution ..... 329
Chemical potential of real solutions: the activity and the reference potential ..... 330
Chapter 17 Chemical equilibrium ..... 335
Introduction ..... 335
Reactants and products ..... 336
Stable and metastable chemical equilibrium ..... 337
The extent of reaction and the composition of a reacting mixture ..... 339
The extent of reaction ..... 339
Mass conservation ..... 341
Molar fractions ..... 341
Examples of the use of the extent of reaction ..... 342
Some properties of the extent of reaction ..... 345
The equilibrium conditions and the direction of a reaction ..... 346
The equilibrium conditions ..... 346
The direction of a chemical reaction ..... 347
Chemical affinity of a reaction ..... 348
Geometric interpretation ..... 349
How to use affinity to answer practical chemistry questions ..... 351
The equilibrium condition in terms of chemical potentials and equilibrium constant ..... 352
The reaction affinity in terms of chemical potential ..... 352
The affinity of a reaction for ideal mixtures ..... 353
The equilibrium conditions for real mixtures ..... 356
Chapter 18 Chemical equilibrium: the connection between the equilibrium constant and composition ..... 359
Introduction ..... 359
How to calculate the equilibrium constant from a measurement of the equilibrium concentration of one species ..... 361
How to calculate the equilibrium composition when you know the equilibrium constant and the initial number of moles ..... 363
The dependence of the extent of reaction on the initial number of moles ..... 365
The role of the initial number of moles ..... 365
Supplement 18.1. Another example of composition calculations ..... 371
Supplement 18.2. A second example and error analysis ..... 373
Supplement 18.3. The direction of a reaction ..... 379
A metastable state ..... 381
Chapter 19 Chemical equilibrium: how to calculate $K$ from $\Delta G^{0}=-R T \ln K$ ..... 383
Calculate $\Delta G^{0}(T, p)$ from $\Delta G$ of formation of the compounds ..... 384
An analogy with $\Delta H$ ..... 384
How to calculate $\Delta G^{0}$ ..... 385
Calculate $\Delta G^{0}$ from $\Delta G^{0}(T, p)=\Delta H^{0}(T, p)-T \Delta S^{0}(T, p)$ :
the method ..... 389
Calculation of $\Delta H^{0}(T, p)$ ..... 391
Calculation of $\Delta S^{0}$ ..... 391
Calculate $\Delta G^{0}$ from $\Delta G^{0}=\Delta H^{0}-T \Delta S^{0}$ : the change of $K$ with temperature ..... 393
Calculation of $\Delta H^{0}$ ..... 394
Calculation of $\Delta S^{0}(T, p)$ ..... 396
Calculation of $\Delta G^{0}(T, p)$ ..... 397
Calculate $\Delta G^{0}$ and $K$ : the change of equilibrium constant with pressure ..... 398
Calculation of $\mathcal{I}_{H}\left(\mathrm{H}_{2} \mathrm{O} ; 1000 \mathrm{~K}, \mathrm{p}\right)$. ..... 400
Numerical results for the molar volumes and $\mathcal{I}_{H}$ ..... 402
Calculation of $\mathcal{I}_{S}(i ; 1000 \mathrm{~K}, p)$ ..... 402
Calculate $\Delta G^{0}(T, p)$ from $\Delta G^{0}(T, p)=\sum_{i} \nu(i) \mu^{0}(i ; T, p)$ ..... 404
Problems ..... 406
Chapter 20 Chemical equilibrium: dependence of equilibrium constant on temperature and pressure ..... 409
The change of the equilibrium constant $K$ with temperature and pressure: the equations ..... 410
The change of equilibrium constant with temperature ..... 410
The change of equilibrium constant with pressure ..... 411
Le Chatelier's Principle ..... 411
The formulation of the principle ..... 411
The derivation of the principle ..... 412
Calculations of the change of the equilibrium constant $K$ with temperature ..... 414
The equilibrium composition at different temperatures and initial compositions ..... 419
The change of the equilibrium constant $K$ with pressure ..... 423
The Use of $(\partial \ln K / \partial p)_{T, n}=-\Delta V^{0} / R T$ (Eq. 20.5) ..... 423
Calculation of the molar volumes ..... 425
Calculation of $\mathcal{I}_{v}(i ; T=1000 \mathrm{~K}, p)$ ..... 426
Calculation of the equilibrium constant at various pressures ..... 427
How to calculate the change of equilibrium constant when both the temperature and pressure are changed ..... 428
Summary ..... 430
Chapter 21 Chemical equilibrium of coupled reactions ..... 431
Introduction ..... 431
Mass balance and equilibrium conditions for coupled reactions ..... 432
Mass balance ..... 432
Equilibrium conditions ..... 432
The equilibrium constants ..... 434
The calculation of $\Delta G_{1}^{0}, \Delta G_{2}^{0}, K_{1}$, and $K_{2}$ ..... 435
Calculation of equilibrium composition for coupled reactions ..... 435
The molar fractions ..... 436
The number of moles ..... 436
The equilibrium constants ..... 439
Calculation of the equilibrium extents of reaction ..... 440
Equilibrium composition ..... 440
Some interesting complications for heterogeneous reactions ..... 440
Generalization ..... 441
Stoichiometric coefficients $\nu(i, \alpha)$ ..... 442
Number of moles and molar fractions ..... 442
The equilibrium constants ..... 443
Another application ..... 444
The results of the calculations ..... 444
Using Le Chatelier's principle ..... 447
Chapter 22 Phase transitions in one-component systems: the phenomena ..... 451
Introduction ..... 451
The phenomena taking place during a phase transition ..... 452
This process is reversible ..... 455
The coexistence curve ..... 455
The complete phase diagram ..... 457
How we use phase diagrams ..... 459
The vapor pressure ..... 459
Chapter 23 Phase transitions in one-component systems: the equilibrium conditions ..... 463
The equilibrium condition for coexisting phases ..... 463
The equilibrium (coexistence) condition ..... 464
How to use this equation ..... 465
Phase stability ..... 466
The analogy to a chemical reaction ..... 468
The Clapeyron equation ..... 468
The entropy of transformation is connected to the heat of transformation ..... 471
Supplement 23.1. The evaporation of droplets and bubbles, and the mysteries of nucleation ..... 472
There is an interface between the phases ..... 472
The stability of a liquid droplet ..... 473
The phase transition is a change of radius ..... 474
If $\mu(\mathrm{g})<\mu(\ell)$, the droplet is unstable ..... 475
The strange "stability" when $\mu(\ell ; T, p)<\mu(\mathrm{g} ; T, p)$ ..... 476
A metastable equilibrium ..... 477
Nucleation ..... 478
Heterogeneous nucleation ..... 479
Chapter 24 Phase transitions in one-component systems: how to use the equilibrium conditions ..... 481
Introduction ..... 481
Transitions involving two condensed phases ..... 483
Melting ..... 483
An example of a solid-solid phase transformation ..... 484
Transitions involving one condensed phase and one vapor phase ..... 487
A simplified theory ..... 488
Using the Clapeyron equation to calculate the vapor pressure of $\mathrm{NH}_{3}$ ..... 495
Another kind of phase diagram ..... 497
Chapter 25 Phase equilibria in binary systems: the phenomena ..... 501
Introduction ..... 501
The independent variables ..... 502
How to make a constant-pressure phase diagram for the liquid-vapor equilibrium in a two-component system ..... 504
Making a constant-pressure phase-diagram ..... 504
The full liquid-vapor phase diagram at constant pressure ..... 509
How much material is there in each coexisting phase ..... 511
Systems with an azeotrope ..... 514
How to make a constant-temperature liquid-vapor phase diagram ..... 516
Chapter 26 Equilibrium conditions for binary systems with two phases: application to vapor-liquid equilibrium ..... 519
Introduction ..... 519
A metastable equilibrium ..... 477
Nucleation ..... 478
Heterogeneous nucleation ..... 479
Chapter 24 Phase transitions in one-component systems: how to use the equilibrium conditions ..... 481
Introduction ..... 481
Transitions involving two condensed phases ..... 483
Melting ..... 483
An example of a solid-solid phase transformation ..... 484
Transitions involving one condensed phase and one vapor phase ..... 487
A simplified theory ..... 488
Using the Clapeyron equation to calculate the vapor pressure of $\mathrm{NH}_{3}$ ..... 495
Another kind of phase diagram ..... 497
Chapter 25 Phase equilibria in binary systems: the phenomena ..... 501
Introduction ..... 501
The independent variables ..... 502
How to make a constant-pressure phase diagram for the liquid-vapor equilibrium in a two-component system ..... 504
Making a constant-pressure phase-diagram ..... 504
The full liquid-vapor phase diagram at constant pressure ..... 509
How much material is there in each coexisting phase ..... 511
Systems with an azeotrope ..... 514
How to make a constant-temperature liquid-vapor phase diagram ..... 516
Chapter 26 Equilibrium conditions for binary systems with two phases: application to vapor-liquid equilibrium ..... 519
Introduction ..... 519
The equilibrium conditions for two coexisting phases in a binary system ..... 520
Derivation of the equilibrium condition ..... 520
The number of independent variables ..... 522
The phase rule ..... 523
Application to liquid-vapor equilibrium: ideal mixtures ..... 524
From equilibrium conditions to phase diagrams ..... 524
Phase diagrams for ideal binary mixtures ..... 525
Replace $\mu_{i}^{0}(g)$ and $\mu_{i}^{0}(\ell)$ with measurable quantities ..... 525
Raoult's Law ..... 526
The vapor pressure $p_{i}^{0}(T)$ of the pure compound ..... 527
Calculation of the dew line and bubble line for a mixture of carbon disulphide and benzene ..... 529
The dew line ..... 529
The bubble line ..... 529
Numerical calculations and comparison ..... 530
Supplement 26.1. The liquid-vapor equilibrium when the
liquid is a real solution and the vapor is an ideal mixture of ideal gases ..... 535
Activity coefficients ..... 536
The dependence of activity coefficient on molar fraction ..... 537
How to calculate the phase diagram at constant temperature if you know the activity coefficients ..... 538
The calculation of the activity coefficients from data on liquid-vapor equilibrium ..... 541
What is wrong with the Margules equation? ..... 541
Chapter 27 Electrolyte solutions ..... 547
Introduction ..... 547
Electrolyte solutions ..... 547
Long-range interactions ..... 548
Mass balance and independent variables ..... 550
Notation, mass balance, and charge conservation ..... 550
Charge neutrality ..... 551
Equilibrium conditions ..... 552
The change in Gibbs free energy ..... 552
A new set of variables ..... 553
The dissociation equilibrium ..... 554
Equilibria involving two phases ..... 555
A discussion of various chemical potentials ..... 557
Why $\mu(+)$ and $\mu(-)$ are not relevant individually ..... 558
Activity and activity coefficient ..... 559
Molality ..... 559
The definition of activity in the molality scale ..... 561
The chemical potential of the electrolyte ..... 562
The Debye-Hückel theory of electrolyte solutions ..... 566
Formulae and use ..... 566
Chapter 28 Galvanic cells: phenomena ..... 571
Introduction ..... 571
Galvanic cells ..... 572
How to make a Daniell cell ..... 572
Daniell cell: the cell reactions ..... 573
Daniell cell: the half reaction at the Cu electrode ..... 574
Daniell cell: the half reaction at the Zn electrode ..... 575
Contact potentials ..... 576
At equilibrium, the voltage inside each conducting phase is constant (in space) ..... 577
Daniell cell in an open circuit ..... 578
Daniell cell in a closed circuit ..... 580
The battery turns chemical energy into electric work ..... 580
Some practice with cell symbols ..... 582
Electrolysis ..... 585
Supplement 28.1. Fuel cells ..... 586
A modern fuel cell ..... 590
The electrolyte ..... 592
The cathode ..... 592
The macro factors ..... 594
Supplement 28.2. A brief history of electrolytic galvanic cells ..... 595
Supplement 28.3. One- and two-euro coins ..... 596
Chapter 29 Galvanic cells: equilibrium conditions ..... 597
Introduction ..... 597
The equilibrium conditions for a charged species in two conducting phases in contact ..... 598
A review of the thermodynamics of mixtures ..... 600
Electrolyte solutions in the absence of an electric field ..... 601
Electrolyte solutions in the presence of an electrostatic potential ..... 601
The change of the Gibbs free energy ..... 603
The equilibrium conditions for charged particles in two adjoining phases ..... 603
The contact potential of two metals ..... 603
The equilibrium conditions for a galvanic cell ..... 605
When a galvanic cell is in equilibrium ..... 605
The equilibrium condition in a cell: example ..... 605
The interpretation of the equilibrium condition ..... 608
The equilibrium composition in the cell ..... 609
The determination of the standard electromotive force $E_{0}$ ..... 612
The experimental determination of $E_{0}$ ..... 612
Determination of $E_{0}$ for the Cell Pt(I), $\mathrm{H}_{2}(1 \mathrm{~atm})|\mathrm{HCl}(\mathrm{m})| \mathrm{Hg}_{2} \mathrm{Cl}_{2}(\mathrm{~s})$ ..... 614
Determine the standard emf of the Cell Pt(I), $\mathrm{H}_{2}$ (1 atm) $|\mathrm{HCl}(\mathrm{m})| \mathrm{HCl}(\mathrm{m})|\mathrm{AgCl}(\mathrm{s}), \mathrm{Ag}| \mathrm{Pt}(\mathrm{II})$ ..... 615
Going beyond the Debye-Hückel theory ..... 618
Half-cell electromotive force ..... 618
The rules for defining and using standard half-cell emfs ..... 619
Why half-cell emfs are useful ..... 621
The propensity of an oxidation-reduction reaction ..... 623Why the rule giving the cell from the half-cellemfs works624
The use of electromotive-force measurements to determine the activity coefficients of an electrolyte solution ..... 626
Using emf measurements to determine activity coefficients ..... 626
The activity coefficient $\gamma( \pm$; HCl) from the electromotive force of the cell Pt(I), $\mathrm{H}_{2}(1 \mathrm{~atm})|\mathrm{HCl}(\mathrm{m})| \mathrm{AgCl}(\mathrm{s})$ $|\mathrm{Ag}| \mathrm{Pt}(\mathrm{II})$ ..... 627
The use of the activity coefficients of electrolytes to calculate how the emf of a cell changes with the molality of the electrolyte solution ..... 630
The connection between the equilibrium composition of a reaction performed in a cell and that of the same reaction performed in a beaker ..... 632
A review of the results needed ..... 633
The gas-liquid equilibrium also matters ..... 634
Developing the equilibrium conditions ..... 635
Using measurements on the open-circuit cell to calculate the gas composition in the short-circuited cell ..... 638
The composition and the partial pressures ..... 639

## Appendices

A1. Conversion factors for pressure units ..... 645
A2. Ethane data ..... 645
A3. Gas constant $R$ in units of energy $/ \mathrm{mol} \mathrm{K}$ ..... 650
A4. van der Waals constants ..... 650
A5. Value of the constants appearing in the Beattie-Bridgeman equation ..... 651
A6. The value of the constants appearing in the Benedict-Webb-Rubin equation ..... 652
A7. Units for work, energy, and heat ..... 655
A8. The dependence of heat capacity on temperature ..... 655
A9. Thermodynamic properties at several temperatures and 1 bar ..... 658
Further Reading ..... 671
Index ..... 675

