
Contents

Notation	xiii
1 Introduction	1
1.1 The scope and nature of chemical thermodynamics	1
1.2 Equilibrium in mechanical systems	2
1.3 Reversibility and equilibrium	4
1.4 Why we need thermodynamics	6
1.5 The mole	8
1.6 The perfect gas	9
2 Energy	10
2.1 Work	10
2.2 Heat and temperature	12
2.3 Measurement of temperature	12
2.4 Heat and molecular motion	13
2.5 Conservation of energy	14
2.6 State functions: a digression	16
2.7 Enthalpy	18
2.8 Heat capacity	19
Problems	20
3 Entropy and equilibrium	21
3.1 Reversibility and equilibrium: a recapitulation	21
3.2 Condition of equilibrium	21
3.3 Entropy	23
3.4 Entropy as a state function	25
3.5 Entropy of expansion of a gas	26
3.6 Entropy changes accompanying heat flow	27
3.7 Entropy and equilibrium	27
3.8 A cosmological aside	28
3.9 Entropy as a function of pressure and temperature	28
3.10 Molecular basis of entropy	30
3.11 Statistical basis of the Second Law	32
3.12 Magnitudes of entropy changes	32
3.13 Heat engines	33
Problems	35

4	Equilibrium in chemical systems	36
4.1	Free energy	36
4.2	Gibbs free energy	37
4.3	Pressure-dependence of free energy	40
4.4	Temperature variation of free energy	41
4.5	Phase equilibria	42
4.6	Clapeyron equation	44
4.7	Clausius–Clapeyron equation	45
4.8	The vapour pressure of liquids	46
4.9	Chemical potential	48
4.10	Chemical potential and free energy	49
4.11	Equilibrium between gaseous reactants	51
4.12	Temperature-dependence of equilibrium constants	55
4.13	Effect of pressure on equilibrium constants	57
4.14	Basic results of chemical thermodynamics	59
4.15	Le Chatelier's Principle	61
	Problems	62
5	Determination of thermodynamic quantities	63
5.1	Hess's Law	63
5.2	Standard enthalpies of formation	64
5.3	Average bond energies	65
5.4	Temperature dependence of enthalpy changes	66
5.5	Standard free energies of formation	67
5.6	Determination of free-energy changes	68
5.7	Determination of entropies of substances	69
5.8	Example of the determination of thermodynamic quantities	70
5.9	Calculation of thermodynamic quantities at temperatures other than 298 K	76
5.10	Ellingham diagrams	77
5.11	Free-energy functions	79
	Problems	80
6	Ideal solutions	82
6.1	The ideal solution	82
6.2	Properties of truly ideal solutions	85
6.3	Mixtures of liquids	86
6.4	Ideal solutions of solids in liquids	88
6.5	Ideal dilute solutions	90
6.6	Colligative properties	91
6.7	Freezing-point depression	92
6.8	Elevation of boiling point	96
6.9	Osmotic pressure	99
6.10	Properties of the solute in dilute solutions	100
6.11	Solubility of solids	102
	Problems	103

7	Non-ideal solutions	104
7.1	The concept of activity	104
7.2	Activity of solids in liquids	106
7.3	Activity in aqueous solutions	107
7.4	Chemical equilibria in solution	110
7.5	Electrochemical cells	112
7.6	Standard electrode potentials	115
	Problems	119
8	Thermodynamics of gases	120
8.1	Expansion of a perfect gas	120
8.2	Irreversible expansion	121
8.3	Equation of state of gases	123
8.4	Joule–Thomson experiment	125
8.5	Imperfect gases: fugacity	126
8.6	Calculation of fugacities	128
	Problems	129
9	Molecular basis of thermodynamics	130
9.1	Energy levels	130
9.2	Microstates	133
9.3	The Boltzmann factor	134
9.4	Behaviour of heat capacity	137
9.5	Partition functions	140
9.6	Entropy and the partition function	141
9.7	Calculation of the translational partition function	145
9.8	The rotational partition function	147
9.9	Vibrational partition function	148
9.10	Evaluation of the properties of gaseous nitrogen	149
9.11	Chemical equilibrium	150
	Problems	154
	Answers to problems	155
	Appendix 1: Thermochemical data at 298.15 K	156
	Appendix 2: Thermodynamic data for ions in aqueous solution at 298.15 K	159
	Further reading	160
	Periodic table of elements	161
	SI units and list of physical constants	162
	Index	163