
Contents

Preface	xi
Notations and Symbols	xv
Chapter 1. Physico-Chemical Transformations and Equilibria	1
1.1. Characteristic parameters of physico-chemical transformations	1
1.1.1. Balance equation of a transformation	1
1.1.2. Values associated with a transformation	2
1.1.3. Standard values associated with a transformation	3
1.1.4. Extent and rate of a transformation	3
1.2. Entropy production during the course of a transformation in a closed system	4
1.3. Affinity of a transformation	5
1.3.1. Definition	5
1.3.2. Affinity and characteristic functions.	6
1.3.3. Affinity and chemical potentials	7
1.3.4. Affinity, reaction quotient and activities	8
1.3.5. Total differential of the affinity in variables Y_i, X_m, ξ	9
1.3.6. Derivatives of the affinity in relation to the extent and the chemical potentials	11
1.4. De Donder's inequality – direction of the transformations and equilibrium conditions	12
1.5. Heats of transformation.	14
1.5.1. Heat of transformation at constant pressure and temperature	15

1.5.2. Heat of transformation at constant volume and temperature	16
1.5.3. Variations in the heat of transformation at constant pressure with changing temperature – Kirchhoff relation	17
1.6. Set of points representing the equilibrium states of a transformation	18
1.7. Closed systems accommodating multiple reactions	19
1.8. Direction of evolution and equilibrium conditions in an open system	20
1.9. Azeotropic transformations	21
Chapter 2. Properties of States of Physico-Chemical Equilibrium	25
2.1. Laws of displacement of an equilibrium	25
2.1.1. General form of the displacement laws	25
2.1.2. Influence of a temperature disturbance	26
2.1.3. Influence of a pressure disturbance	27
2.1.4. Influence of the addition of a component	27
2.1.5. Influence of the addition of an inert component	32
2.2. Properties of all the equilibria in a system	33
2.2.1. Property of the set of balance equations of a system	34
2.2.2. Linear combinations of balance equations	36
2.2.3. Base of the vector space of the balance equations – Jouguet criteria	37
2.3. Phase laws	41
2.3.1. Reminder of Gibbs' phase rule	41
2.3.2. Duhem's phase rule in closed systems	42
2.3.3. Comparison between the Gibbs variance and the Duhem variance	44
2.4. Indifferent states	44
2.4.1. Definition	45
2.4.2. Condition of indifference of a state	45
2.4.3. Set of indifferent points of equilibrium	47
2.4.4. Gibbs–Konovalov theorem	47
2.5. Thermodynamically-equivalent systems	48
2.6. Stability of equilibria	48
2.6.1. De Donder's general stability condition	49
2.6.2. Stability of a system with unilateral variations	49
2.6.3. Stability of a system with bilateral variations	51

2.6.4. Conditions of bilateral stability expressed in terms of chemical potentials	53
Chapter 3. Molecular Chemical Equilibria	55
3.1. Law of mass action – equilibrium constants	55
3.1.1. Expression of the law of mass action	55
3.1.2. Different forms of the law of mass action	57
3.1.3. Use of solution models and application of the law of mass action	62
3.1.4. Systems composed of a set of equilibria	63
3.1.5. Unit of the equilibrium constants	64
3.1.6. Variations of the equilibrium constants with temperature	64
3.1.7. Influence of the choice of reference pressure on the equilibrium constant	66
3.1.8. Dissociative dissolution of a gas in a solid	67
3.2. Graphical representations of equilibria – pole diagrams	69
3.2.1. Principle of the pole diagram	69
3.2.2. Influence of a temperature change on a pole diagram	70
3.2.3. Pole diagrams of two reactions in the same family	72
3.3. Representation of the evolution of an equilibrium with the temperature.	73
3.3.1. Diagram in van 't Hoff coordinates	73
3.3.2. Ellingham diagrams	74
3.4. Binary diagrams for chemical equilibrium	88
3.5. Ternary diagrams of chemical equilibria.	89
3.5.1. Mode of representation	90
3.5.2. Molar fractions at equilibrium and initial composition	93
3.5.3. Iso-Q curves in perfect solutions	95
3.5.4. Iso-composition curves in perfect solutions	98
3.6. Quaternary diagrams of chemical equilibria	100
Chapter 4. Determination of the Values Associated with Reactions – Equilibrium Calculations	105
4.1. Reminders of a few thermodynamic relations	105
4.2. Enthalpies of reaction – thermochemistry	110
4.2.1. Experimental determination of the reaction enthalpies by calorimetry	111
4.2.2. Calculation of the standard enthalpy at another temperature	111

4.2.3. Influence of the pressure on the reaction enthalpies	111
4.2.4. Determination of the reaction enthalpies by calculation on the basis of other thermodynamic data	112
4.2.5. Enthalpies of formation	114
4.2.6. Enthalpies of combustion	116
4.2.7. Dissociation energy, bond energy and enthalpies of formation.	119
4.3. Reaction entropies	126
4.3.1. Planck's hypothesis – calculation of the calorimetric entropies	126
4.3.2. Spectroscopic determination of entropies – absolute entropies	128
4.3.3. The third law	128
4.4. Specific heat capacities	131
4.4.1. Calorimetric measurements of the specific heat capacities	131
4.4.2. Spectral measurements of the specific heat capacities	134
4.5. Experimental determination of the equilibrium constants	134
4.6. Calculation of the equilibrium constants on the basis of other thermodynamic data	136
4.6.1. Calculation of the equilibrium constants – method 1.	137
4.6.2. Calculation of the equilibrium constants – method 2.	137
4.6.3. Calculation of the equilibrium constants – method 3.	137
4.6.4. Calculation of the equilibrium constants – method 4.	138
4.6.5. Calculation of the equilibrium constants – method 5.	138
4.7. Determination of the equilibrium constants on the basis of spectral data and statistical thermodynamics	140
4.8. Thermodynamic tables and databanks	140
4.9. Estimation of thermodynamic data	142
4.9.1. Method of evaluating the energies of dissociation by spectroscopy	143
4.9.2. Group contribution methods	143
4.10. Thermodynamic calculations for complex systems.	146
4.10.1. Definition of the system	147
4.10.2. Output mode – graphical representation.	147

4.10.3. Calculation method based on the equilibrium constants	148
4.10.4. Method of minimization of the Gibbs energy function	149
Appendices	151
Appendix 1	153
Appendix 2	163
Bibliography	181
Index	185