Contents

	•	to second edition to first edition	<i>page</i> xii xiii
1	Basic c	concepts of thermodynamics	1
	1.1 Ex	sternal state variables	1
	1.2 In	ternal state variables	3
		ne first law of thermodynamics	5
		eezing-in conditions	9
		eversible and irreversible processes	10
		econd law of thermodynamics	13
		ondition of internal equilibrium	17
		riving force	19
		ombined first and second law	21
		eneral conditions of equilibrium	23
		naracteristic state functions	24
	1.12 Er	ntropy	26
2	Manipu	lation of thermodynamic quantities	30
	2.1 Ev	valuation of one characteristic state function from another	30
	2.2 Int	ternal variables at equilibrium	31
	2.3 Eq	quations of state	33
	2.4 Ex	xperimental conditions	34
	2.5 No	otation for partial derivatives	37
	2.6 Us	se of various derivatives	38
	2.7 Co	omparison between Cv and Cp	40
	2.8 Cł	nange of independent variables	41
	2.9 M	axwell relations	43
3	Systems	s with variable composition	45
	3.1 Cł	nemical potential	45
		folar and integral quantities	46
		ore about characteristic state functions	48
	5.5 141	or acceptance pane imparem	10

	3.4	Additivity of extensive quantities. Free energy and exergy	51
	3.5	Various forms of the combined law	52
	3.6	Calculation of equilibrium	54
	3.7	Evaluation of the driving force	56
	3.8	Driving force for molecular reactions	58
	3.9	Evaluation of integrated driving force as function of	
		T or P	59
	3.10	Effective driving force	60
4	Prac	ctical handling of multicomponent systems	63
	4.1	Partial quantities	63
	4.2	Relations for partial quantities	65
	4.3	Alternative variables for composition	67
	4.4	The lever rule	70
	4.5	The tie-line rule	71
	4.6	Different sets of components	74
	4.7	Constitution and constituents	75
	4.8	Chemical potentials in a phase with sublattices	77
5	Ther	modynamics of processes	80
	5.1	Thermodynamic treatment of kinetics of	
		internal processes	80
	5.2	Transformation of the set of processes	83
	5.3	Alternative methods of transformation	85
	5.4	Basic thermodynamic considerations for processes	89
	5.5	Homogeneous chemical reactions	92
	5.6	Transport processes in discontinuous systems	95
	5.7 5.8	Transport processes in continuous systems	98
	5.8 5.9	Substitutional diffusion Onsager's extremum principle	101 104
	3.9	Onsager's extremum principle	10-
6	Stab	pility	108
	6.1	Introduction	108
	6.2	Some necessary conditions of stability	110
	6.3	Sufficient conditions of stability	113
	6.4	Summary of stability conditions	115
	6.5	Limit of stability	116
	6.6	Limit of stability against fluctuations in composition	117
	6.7	Chemical capacitance	120
	6.8	Limit of stability against fluctuations of	
		internal variables	12:
	6.9	Le Chatelier's principle	123

7	Арр	lications of molar Gibbs energy diagrams	126
	7.1	Molar Gibbs energy diagrams for binary systems	126
	7.2	Instability of binary solutions	131
	7.3	Illustration of the Gibbs-Duhem relation	132
	7.4	Two-phase equilibria in binary systems	135
	7.5 7.6	Allotropic phase boundaries	137
	7.0	Effect of a pressure difference on a two-phase equilibrium	138
	7.7	Driving force for the formation of a new phase	142
	7.8	Partitionless transformation under local equilibrium	144
	7.9	Activation energy for a fluctuation	147
	7.10	Ternary systems	149
	7.11	Solubility product	151
8	Phas	se equilibria and potential phase diagrams	155
	8.1	Gibbs'phase rule	155
	8.2	Fundamental property diagram	157
	8.3	Topology of potential phase diagrams	162
	8.4	Potential phase diagrams in binary and multinary systems	166
	8.5	Sections of potential phase diagrams	168
	8.6 8.7	Binary systems	170 173
	8.8	Ternary systems Direction of phase fields in potential phase diagrams	173
	8.9	Extremum in temperature and pressure	181
9	Mok	ar phase diagrams	185
	9.1	Molar axes	185
	9.2	Sets of conjugate pairs containing molar variables	189
	9.3	Phase boundaries	193
	9.4	Sections of molar phase diagrams	195
	9.5	Schreinemakers' rule	197
	9.6	Topology of sectioned molar diagrams	201
10	Proj	ected and mixed phase diagrams	205
	10.1	Schreinemakers' projection of potential phase diagrams	205
	10.2	The phase field rule and projected diagrams	208
	10.3	Relation between molar diagrams and Schreinemakers'	
		projected diagrams	212
	10.4	Coincidence of projected surfaces	215
	10.5	Projection of higher-order invariant equilibria	217
	10.6 10.7	The phase field rule and mixed diagrams Selection of axes in mixed diagrams	220 223
	10.7	belocition of axes in mixed diagrams	223

		Konovalov's rule General rule for singular equilibria	226 229
11		ction of phase boundaries	233
	11.1	Use of distribution coefficient	233
		Calculation of allotropic phase boundaries	235
		Variation of a chemical potential in a two-phase field	238
		Direction of phase boundaries	240
		Congruent melting points	244
		Vertical phase boundaries	248
	11.7	Slope of phase boundaries in isothermal sections	249
	11.8	The effect of a pressure difference between two phases	251
12	Shan	p and gradual phase transformations	253
	12.1	Experimental conditions	253
		Characterization of phase transformations	255
		Microstructural character	259
		Phase transformations in alloys	261
	12.5	Classification of sharp phase transformations	262
	12.6	Applications of Schreinemakers' projection	266
	12.7	Scheil's reaction diagram	270
	12.8	Gradual phase transformations at fixed composition	272
	12.9	Phase transformations controlled by a chemical potential	275
13	Trans	sformations in closed systems	279
	13.1	The phase field rule at constant composition	279
	13.2	Reaction coefficients in sharp transformations	
		for $p = c + 1$	280
	13.3	Graphical evaluation of reaction coefficients	283
	13.4	Reaction coefficients in gradual transformations	
		for $p = c$	285
	13.5	Driving force for sharp phase transformations	287
	13.6	Driving force under constant chemical potential	291
	13.7	Reaction coefficients at constant chemical potential	294
	13.8	Compositional degeneracies for $p = c$	295
	13.9	Effect of two compositional degeneracies for $p = c - 1$	299
14	Parti	tionless transformations	302
	14.1	Deviation from local equilibrium	302
	14.2	Adiabatic phase transformation	303
	14.3	Quasi-adiabatic phase transformation	305
	14.4	Partitionless transformations in binary system	308

		Partial chemical equilibrium Transformations in steel under quasi-paraequilibrium Transformations in steel under partitioning of alloying elements	311 315 319
15	Limit	of stability and critical phenomena	322
	15.3 15.4	, 6 1	322 325 330 334 338
16	Interfa	aces	344
	16.1 16.2 16.3 16.4 16.5 16.6 16.7 16.8 16.9 16.10 16.11 16.12	Phase equilibrium at fluid/fluid interfaces Size stability for spherical inclusions Nucleation Phase equilibrium at crystal/fluid interface Equilibrium at curved interfaces with regard to composition Equilibrium for crystalline inclusions with regard to composition Surface segregation Coherency within a phase Coherency between two phases	344 345 346 350 351 353 356 359 361 363 366 371
17	Kineti	ics of transport processes	377
	17.1 17.2 17.3 17.4 17.5 17.6 17.7	Local volume change Composition of material crossing an interface	377 381 384 388 390 391 396
18	Metho	ods of modelling	400
	18.1 18.2 18.3 18.4 18.5 18.6 18.7	General principles Choice of characteristic state function Reference states Representation of Gibbs energy of formation Use of power series in <i>T</i> Representation of pressure dependence Application of physical models	400 401 402 405 407 408 410

	18.9 18.10 18.11	Ideal gas Real gases Mixtures of gas species Black-body radiation Electron gas	411 412 415 417 418
19	Mode	lling of disorder	420
	19.1 19.2 19.3 19.4 19.5 19.6 19.7 19.8 19.9	Introduction Thermal vacancies in a crystal Topological disorder Heat capacity due to thermal vibrations Magnetic contribution to thermodynamic properties A simple physical model for the magnetic contribution Random mixture of atoms Restricted random mixture Crystals with stoichiometric vacancies Interstitial solutions	420 423 425 429 431 434 436 437
20		ematical modelling of solution phases	441
	20.3 20.4 20.5 20.6	Ideal solution Mixing quantities Excess quantities Empirical approach to substitutional solutions Real solutions Applications of the Gibbs-Duhem relation Dilute solution approximations Predictions for solutions in higher-order systems Numerical methods of predictions for higher-order systems	441 443 444 445 448 452 454 456 458
21	Soluti	ion phases with sublattices	460
	21.3	Sublattice solution phases Interstitial solutions Reciprocal solution phases Combination of interstitial and substitutional solution Phases with variable order Ionic solid solutions	460 462 464 468 469 472
22	Physi	ical solution models	476
	22.1 22.2	Concept of nearest-neighbour bond energies Random mixing model for a substitutional solution	476 478

22.3 Deviation from random distribution

Short-range order

22.4

479

482

22.5	Long-range order	484
22.6	Long- and short-range order	486
22.7	The compound energy formalism with short-range order	488
22.8	Interstitial ordering	490
22.9	Composition dependence of physical effects	493
Refere	496	
Index		499