## MATERIALS THERMOCHEMISTRY

Sixth Edition

by

## O. KUBASCHEWSKI

DR PHIL. HABIL. DRS. H.C.

Technische Hochschule, Aachen

C. B. ALCOCK

Ph.D. A.R.C.S. D.Sc. F.R.S.C.

University of Notre Dame, Indiana

P. J. SPENCER

Ph.D.

Technische Hochschule, Aachen



## **PERGAMON PRESS**

OXFORD

**NEW YORK** 

SEOUL ·

TOKYO

## **Contents**

Notation			xi
1.	Tl	ne Theoretical Basis	
	1.	The mass action law	1
	2.	Thermodynamic functions	3
		A. The equilibrium constant and thermodynamic functions	3 4
		B. Heat content and enthalpy of formation	
		C. Temperature dependence of the enthalpy of reaction	8
		D. Entropy	13
	2	E. Gibbs energy	17
	3.	Solutions A. Portiol molor Cibbs anarry	27 27
		<ul><li>A. Partial molar Gibbs energy</li><li>B. Vapour pressures and partial Gibbs energies</li></ul>	30
		C. The calculation of integral values from partial molar thermochemical	30
		data	34
		D. Dilute solutions	44
		1. Raoult's law	44
		2. Henry's law	45
		E. Atomistics and solution thermodynamics	47
		F. Regular solutions	50
		1. Calculation of activities using equilibrium diagrams	50
		2. Spinodal decomposition	51
		3. Order-disorder transformation	53
		G. Non-regular solutions	53
		H. Ternary solutions	56
2.	E	xperimental Methods	
	1.	Calorimetric methods	65
		A. Measurement of temperature	66
		1. Mercury-in-glass thermometers	67
		2. Platinum resistance thermometers	67
		3. Thermocouples	68
		4. Thermistors	68
		5. Optical pyrometers	68
		B. Determination of water equivalent	68
		1. Heat contents and heat capacities	70 79
		2. Enthalpies of fusion and transformation	83
	2.	3. Enthalpies of reaction and formation Equilibria with a gaseous phase	95
	4.	The equilibrium constant for vaporisation reactions	96 96
		A. Static methods for the measurement of vapour pressure	97
		State memods for the measurement of rapeur pressure	vii

v	i	i	i	Contents	

		1. Manometric methods	97
		2. Static methods using radiation	98
		B. Gas-condensed phase equilibria in a closed system	100
		1. The dew-point method	100
		2. The isopiestic method	100
		3. Tensi-eudiometer measurements	102
		4. Sievert's method	104
		C. Dynamic vapour pressure methods	106
		1. The boiling point method	106
		2. The transportation method	108
		D. Other heterogeneous equilibria	112
		1. Reaction between a gas phase and a condensed phase	113
		E. Methods based on rates of evaporation	120
		1. The Knudsen effusion method	121
		2. The Knudsen cell-mass-spectrometer combination	125
		3. The Langmuir vaporisation method	133
		4. Torsion effusion	136
		5. Vapour transpiration	138
	3.	Electromotive forces	140
		A. Liquid electrolytes	143
		1. Aqueous solutions	143
		2. Molten salt electrolytes	143
		B. Solid electrolytes	146
		1. Glass electrolyte	146
		2. Solid oxide electrolytes	148
		3. Other cells	159
3.	Th	e Estimation of Thermochemical Data	
	1.	Heat capacities	163
		A. Gaseous atoms and molecules	163
		B. Solids	164
		C. Liquids	167
		D. Some average values	168
	2.	Enthalpies and entropies of transformation, fusion and evaporation	169
		A. Evaporation	169
		B. Fusion	169
	3.	Entropy and entropy changes	171
		A. Standard entropies	171
		1. Solids	171
		2. Gases	174
		B. Entropies of mixing of non-metallic solution phases	177
	4.	Enthalpies of formation	179
		A. General	180
		B. Homologous series	180
		C. Empirical relations	182
		1. Polyvalent metal oxides	182
		2. Metal oxyhalide compounds	182
		3. Double salts with the formula $MX_aY_b$	183
		4. Oxides, carbonates, sulphates, hydroxides and nitrates	184
		5. Halides	185
		D. Enthalpies of formation of double oxides	185
		1. Plots involving the ratio of ionic charge to ionic radius	185
		2. Statistical analysis methods	187
		3. Le Van's method	187
		4. Comparison of data for similar compounds	188
		E. Volume change and enthalpy of formation	189

		Contents	ix
		F. Enthalpy of solution	190
		G. The packing effect	192
		H. Temperature increase during compound formation	194
	5.	Thermodynamic properties of alloys	197
		A. Calculations using the Wigner-Seitz model of metals	197
		B. Properties of mixing from "Free volume" theory	199
4.	Ex	camples of Thermochemical Treatment of Materials Problems	
	1.	Iron and steelmaking	203
		A. Deoxidation of steel	203
		1. Deoxidation with silicon	203
		2. Deoxidation with aluminium	204
		B. The decarburisation of iron-chromium-carbon and iron-silicon-carbon	
		liquid alloys	205
		C. Chill factors	208
		D. "Window" for liquid calcium aluminates in continuous casting	209
		E. Precipitation of carbide and nitride phases from dilute solution in alloy steels	210
	2.	Non-ferrous metallurgy	212
	2.	A. Aluminothermic type reactions	212
		1. The production of uranium by reduction of its fluoride with calcium	
		and magnesium	212
		2. The production of manganese and chromium by the aluminothermic	
		process	214
		B. The chlorination of metal oxides	215
		C. Refining of lead	216 218
	3.	The removal of zinc from lead     Stability and production of ceramics	218
	Э.	A. The free evaporation of an oxide ceramic in vacuo	218
		B. Metal-refractory interaction	220
		C. Electrochemical cells and the stabilities of ceramics	225
		D. Equilibrium phase relations relevant to the production of oxide super- conductor materials	226
	4.	Chemical vapour deposition (CVD) and physical vapour deposition (PVD)	
		processes	227
		A. CVD of ultra-pure silicon	227
		B. Vapour phase transport of silicon carbide	228
		C. Prediction of metastable phase formation during PVD of mixed coating	
	_	materials	231
	5.	Corrosion	231
	_	A. The oxidation of iron-chromium alloys	231 235
	0.	Environmental and energy problems  A. Calculation of hazardous emissions during sintering of ores	235
		B. Incineration of waste in a molten iron bath	237
		C. Thermodynamic conditions for formation of dioxin in waste incineration	239
		D. Energy conservation in waste incineration	241
	7.	Assessment of standard values	241
		A. A pure stoichiometric substance—silicon monoxide	241
		B. A system exhibiting wide solution ranges—chromium-nickel	247
	8.	Calculation of metallurgical equilibrium diagrams	253
5.	Th	ermochemical Data	257
Inde	2X		361