Contents

	Prefac	ce	<i>page</i> vii
	Units of pressure		xv
1			1
	1.1	General	1
	1.2	Historical survey	4
2	Press	ure and some physical properties of one-phase	
	sys	tems	13
	2.1	The compression of pure gases and gas mixtures	14
		The compression of pure liquids and liquid mixtures	18
		Pressure and the viscosity of gases and liquids	22
	2.4	Pressure and the dielectric constants of gases and	
		liquids	25
	2.5	•	27
	2.6	The electrical conductance of ionic solutions at high	
		pressures	31
	2.7	The compression of solids	34
3	Press	sure and phase equilibria	40
	3.1	General	40
	3.2	Liquid-vapour equilibria in systems of one component	ıt 40
	3.3		41
		Solid-solid equilibria	51
		Gas-liquid equilibria in two-component systems	52
		Gas hydrates	62
		Liquid-liquid equilibria at high pressures	63
	3.8	The solubility of solids in liquids and gases at high	
		pressures	65
		Gas-polymer systems at high pressures	67
	3.10	Sorption of gases by solids at high pressures	70
4	Equip	oment and techniques for chemical reactions at	
	hig	h pressures	78
	4.1	The general arrangement of equipment for liquid-phas	e 78
	4.2		78 81
	T.4	The strength of thick-watted cylinders	
			ix

· CONTENTS

	4.3	Other components of laboratory high pressure equipment	87
	4.4	The generation of high pressures in liquids and gases	90
	4.5	The measurement of high pressures	92
	4.6	Techniques for the study of reactions in liquids under	
		pressure .	95
	4.7	Techniques for the study of gas reactions at high pressure	98
	4.8	Safety precautions for experimental work at high pressure	98
	4.9	Hydrogen embrittlement and hazards in the use of other compressed gases	100
	4.10	High pressure-high temperature techniques	102
5	Chen	nical equilibria in liquids at high pressures	109
	5.1	The theory of chemical equilibria in liquids	109
	5.2	Pressure effects on chemical equilibria in non-ionic systems	
	5.3	The effects of pressure on ionic equilibria	
6	The e	effects of pressure on reaction rates in liquids	
	6.1	General	
	6.2	Reaction rates at high pressures and the collision theory	
	6.3	Reaction rates at high pressures and the transition state theory	
	6.4	Some general characteristics of ΔV^{\pm}	
	6.5	The contribution to ΔV^{\pm} from the 'solvation' of ionic charges	
	6.6.	Further examples of the relation between ΔV^{\pm} and the ionic-type of a reaction	
	6.7	The effect of variations in reactant structure on the volume of activation	
	6.8	The dependence of ΔV [±] on the nature of the solvent in 'polar' reactions	
	6.9	Volumes of activation for some reactions in water and aqueous solvents—the use of ΔV^{\pm} to determine reaction mechanisms	
	6.10	The volumes of activation and mechanisms of some 'non-polar' reactions	
	6.11	Diffusion-controlled reactions at high pressures	
		A further consideration of the transition state theory of	
		reaction rates at high pressures	166
7	Effec	ts of pressure on some organic reactions in liquids	175
•	7.1	General	175
	7.2	Some condensation reactions of ketones	175
		COLLEGE CONTRACTOR TOWNS OF HOUSE	

CONTENTS

	7.3	The rates and products of some aromatic substitutions at high pressures	
	7.4	Synthesis of the oximes of hindered ketones at high	
	7.1	pressures	184
	7.5	Diene additions (Diels-Alder reactions) at high pressures	184
	7.6	The synthesis of cyclic trimers from nitriles at high	
		pressures	188
	7.7	High pressure reactions of hydrogen sulphide	189
	7.8	The synthesis of quinazolidinediones and formamidines	190
	7.9	Additions to the olefinic double bond at high pressures	191
	7.10	Arbuzov reactions	192
	7.11	The effect of pressure on restricted rotation about a	
		single bond	192
		Olefine-forming elimination reactions at high pressures	193
	7.13	The solvolysis of exo- and endo- bicyclic compounds	
		under pressure	195
		Some isomerizations at high pressures	196
		The hydrolysis and methanolysis of nitriles	198
		Effects of pressure on proteins and related substances	199
	7.17	Some difficulties in the interpretation of pressure effects	200
		in liquid-phase reactions	200
8	The 1	kinetics and thermodynamics of radical addition	
	pol	ymerization at high pressures	206
	8.1		206
	8.2		207
	8.3	The effect of pressure on the dissociation of polymerization	017
		initiators	217
	8.4	The thermodynamics and reversibility of polymerization at high pressures	
	8.5	A comparison of the effects of pressure on the rates of radical polymerization of various monomers	
	8.6	The influence of chain-transfer to the monomer on radical polymerization at high pressures	
	8.7	The effect of pressure on radical co-polymerization	
		reactions	228
	8.8	The effect of polymerization pressure on stereo-	
		regularity	235
9	Furti	ner aspects of polymerization and polymerizability	
-		high pressures	239
		General	239

xii · CONTENTS

	9.2	The polymerizability of some monomers with allylic	
		structures	240
	9.3	Di-substituted ethylenes at high pressures	242
	9.4	Effects of pressure on tri- and tetra- substituted	
		ethylenes	243
	9.5	Dienes and cyclic olefines	244
	9.6	Ionic polymerization at high pressures	245
	9.7	The high pressure polymerization of ethylene	246
	9.8	The polymerization of fluoro-olefines at high pressures	251
	9.9	Some copolymers synthesized at high pressure	252
	9.10	The polymerization of aldehydes at high pressures	254
	9.11	The effect of pressure on ring-opening polymerizations	256
	9.12	The pressure-polymerization of other non-olefinic	
		monomers	257
	9.13	Telomerization reactions under pressure	262
	9.14	Some miscellaneous pressure-polymerizations	263
10	Effec	ts of pressure on the equilibria and kinetics of gas	
		ctions	269
	10.1	Equilibrium constants of gas reactions at high pressures	269
	10.2	The ammonia synthesis equilibrium at high pressures	273
	10.3	Further examples of the effect of pressure on equilibrium in gas reactions	
	10.4	Pressure and the kinetics of the ammonia synthesis reaction	
	10.5	The effect of pressure on the stereochemistry of catalytic hydrogenation	282
	10.6	The kinetics of homogeneous gas reactions at high	
		pressures	283
11	Some	e reactions of gases at high pressures	292
	11.1	General	292
	11.2	Reactions of CO with amines	292
	11.3	Reducing reactions of CO at high pressures	293
	11.4	Reactions of CO ₂ with ammonia and amines	295
	11.5	Some reactions of hydrocarbons at high pressures	296
	11.6	Some syntheses of hydrocarbons at high pressures	298
	11.7	The hydroformylation of olefines	299
	11.8	The carbonylation of dienes at high pressures	301
	11.9	High-pressure syntheses of acids, esters and amides	303
		Reactions of fluorine with alkali metal halides at high	503
	11.10	pressures and temperatures	306

		CONTENTS	X111
12	Reac	tions at very high pressures	310
	12.1	General	310
	12.2	Equipment for generating very high pressures	310
	12.3	Pressure and temperature measurements at very high	
		pressures	316
	12.4	Chemical reactions in molecular solids	318
	12.5	Chemical aspects of diamond synthesis	320
		Reactions analogous to the graphite-diamond transformation	323
	12.7	Very rapid reactions of solids under high pressure	325
	12.8	Silica and silicate minerals at very high pressures	326
	12.9	The study of reactivity and structure under pressure	327
	Nam	e index	335
	Subject index		341