## Contents

## Preface

	Intro	duction	1
	1.1	Generalities	1
	1.2	Classification of solvents	3
	1.3	Some essential thermodynamics and kinetics:	
	88	tendency and rate	4
	1.4	Equilibrium considerations	4
	1.5	Thermodynamic transfer functions	6
	1.6	Kinetics considerations: Collision theory	7
	1.7	Transition-state theory	7
	1.8	Reactions in solution	12
	1.9	Diffusion-controlled reactions	12
	1.10	Reactions in solution and the Transition-State Theory	13
	Proble	ems	16
		ALEGER CHILDRAHOUS	
	The	Introduction: Modelling	18
2	The s	Liter sheet at a tractical a	18
	2.1	Intermolecular potentials	10
	2.2	Activity and equilibrium in non-electrolyte solutions	19
	2.3	Rinetic solvent effects	24
	2.4	Polarity	24
	2.5	Electrostatic forces	24
	2.6	Electrolytes in solution	20
	2.7	Solvation	29
	2.8	Single ion solvation	31
	2.9	Ionic association	32
	2.10	Mixed solvents	31
	2.11	Salt effects	41
	Probl	ems northern Lad of Land States and Lad.	42
3	The	solvent as participant	44
	31	Specific interactions	44
	32	Hydrogen bonding	45
	33	Acids and bases in solvents	45
	34	Brønsted Lowry acids and bases	46
	35	Acidity functions	18
	3.6	General acid/base catalysis and the kinetic solvent	40
	0.0	isotope effect	52
	3.7	Lewis acids and bases	54
	3.8	Hard and soft acids and bases ('USAD')	. 55
	0.0	This and soft acrus and bases ( IDAD )	55

v 14 Unification of additions and redoct

viii Contents

	3.9	Scales of hardness/softness	56
	3.10	Acids and bases in reactive aprotic solvents	60
	3.11	Extremes of acidity and basicity	60
	3.12	Oxidation and reduction	61
	3.13	Acidity/redox diagrams	61
	3.14	Unification of acid/base and redox concepts	63
	Proble	ems	63
	~	new problems have been provided for some of the chapt follower	
	Chen	iometrics: Empirical correlations of solvent effects	66
	4.1	Linear free energy relationships	66
	4.2	Correlations between empirical parameters and	
	Telesin	measurable solvent properties	68
	4.3	Representation of correlation data on	1. And
		the hemisphere	71
	4.4	Some particular cases	73
	4.5	Acidity and basicity parameters	77
	4.6	Softness parameters	80
	4.7	Conclusion	81
		nry (2nd equal to a substantiate Deads and out allow any notice all a	
;	Theo	retical calculations	83
	51	Introduction: Modelling	83
	5.2	Quantum-mechanical methods	84
		5.2.1 Ab initio	84
		5.2.2 Semi-empirical methods	88
		5.2.3 Density-functional theory	88
		5.2.4 The solvent as dielectric	89
	5.3	Statistical-mechanical methods	90
	5.4	Monte Carlo method	92
	5.5	Molecular dynamics	94
	5.6	Solvation calculations	94
	5.7	Integral equation theories	94
	5.8	Some results	95
		5.8.1 Microsolvation	95
		5.8.2 A classic reaction: The $S_N 2$ reaction,	
		gas-phase versus solution	97
		5.8.3 Solvatochromism: Theoretical calculations	99
	5.9	Hydrophobic solvation	101
	Probl	em anoitocratin officiação	103
-	D:	Acids and bases in solvents	104
)	Dipo	ar aprotic solvents	104
	6.1	Introduction and build a state of the state	104
	6.2	Acidities in DMSO and the $H_{-}$ scale in DMSO- $H_2O$ mixtures	104
	6.3	Use of thermodynamic transfer functions	107
	6.4	Classification of rate profile-medium effect reaction types	109
	65	Bimolecular nucleophilic substitution	111

6.0	Proton transfer	1
6.7	$D_2$ -OH <sup>-</sup> exchange	1
7 Som	e other examples: Acidic, basic, chiral,	
solve	ents; ionic liquids, green chemistry	
7.1	Introduction	
7.2	Acidic solvents	-
	7.2.1 An acidic solvent; hydrogen fluoride	
	7.2.2 Reactions in hydrogen fluoride	1
	7.2.3 Electrochemistry in hydrogen fluoride	1
7.3	Basic solvents	1
	7.3.1 A basic solvent, ammonia	1
	7.3.2 A basic solvent, pyridine	
7.4	Chiral solvents	
7.5	Ionic liquids	
	7.5.1 Reactions in ionic liquids; green chemistry	
8 Con	cluding observations	
8 Cone 8.1	cluding observations Choosing a solvent	
8 Cone 8.1 8.2	cluding observations Choosing a solvent Envoi	
8 Cone 8.1 8.2	cluding observations Choosing a solvent Envoi	
8 Cond 8.1 8.2	cluding observations Choosing a solvent Envoi	
8 Cone 8.1 8.2 Append	cluding observations Choosing a solvent Envoi	
8 Con 8.1 8.2 Append	cluding observations Choosing a solvent Envoi	
8 Cond 8.1 8.2 Append Reference	choosing a solvent Envoi ix	
8 Cone 8.1 8.2 Append Reference	choosing a solvent Envoi ix	
8 Cond 8.1 8.2 Append Reference	choosing a solvent Envoi	
8 Cond 8.1 8.2 Append Reference	choosing a solvent Envoi	
8 Cond 8.1 8.2 Append Reference	choosing a solvent Envoi ix	1
8 Cond 8.1 8.2 Append Reference	choosing a solvent Envoi	
8 Cond 8.1 8.2 Append Reference	choosing a solvent Envoi	1
8 Cond 8.1 8.2 Append Reference	choosing a solvent Envoi	1
8 Cond 8.1 8.2 Append Reference	<pre>choosing a solvent Envoi</pre>	
8 Cond 8.1 8.2 Append Reference	<pre>chuding observations Choosing a solvent Envoi  ix ces</pre>	