

CONTENTS

Preface

page xv

CHAPTER I

Introduction – the negative ion of hydrogen (H^-)

1.1	General theoretical considerations	1
1.2	Calculation of negative-ion structure by quantum methods	5
1.3	The hydrogen negative ion	6
	Calculation of the electron affinity	6
	The charge distribution in H^-	11

CHAPTER 2

Ground states of complex atomic negative ions – theoretical considerations

2.1	The states of complex atoms	16
	Electron configurations	16
	States arising from a given configuration	17
2.2	Calculation of the structure and energy of complex atomic negative ions	19
	The Hartree-Fock method	19
	The Hartree-Fock-Roothan (HFR) procedure	23
	Inclusion of correlation	25
	The fluorine negative ion	27
	Electron affinities of alkali metal atoms	28

CHAPTER 3

The electron affinities of the elements

3.1	Experimental methods for measuring electron affinities	31
	From photodetachment	32
	From the threshold frequency for polar photodissociation	32

	From threshold energies for dissociative attachment processes	<i>page</i> 33
	From threshold energies for polar dissociation of molecules by electron impact	33
	From the variation with frequency of the affinity continuum	33
	From measurements of ion currents arising from reactions at a hot filament	34
	From the energy relations involved in cyclic processes	46
3.2	Empirical methods	48
	Isoelectronic extrapolation	49
	Horizontal extrapolation	49
	Results for atoms of the first two short periods	60
	Electron affinities of heavier elements	61
	 CHAPTER 4	
	Atomic negative ions – excited states – autodetachment; general account	
4.1	Bound excited states of negative ions	66
4.2	Continuum states of negative ions	67
	Relation to elastic scattering by a centre of force	68
	Convergence of the phase shifts	71
	Relation of phase shifts to time delay in scattering	72
	Wave functions describing electron scattering by atoms	73
4.3	Negative-ion formation by excited atoms – autodetachment	77
	Lifetime of an autodetaching state	79
	The observation of non-metastable autodetaching states	81
	Autodetaching states and elastic scattering of electrons by atoms	82
	Autodetaching states and inelastic scattering of electrons by atoms	90
	Autodetaching states and photodetachment	92
	Calculation of the energy of doubly-excited states of negative ions	92
	Summary	95
4.4	One-body or shape resonances	97
4.5	Siegert states	104

4.6	Type I and type II resonance states	<i>page</i> 107
4.7	Experimental study of autodetaching and shape resonance states from resonance effects in electron-atom collisions	107
	Transmission experiments	109
	Measurements of energy and angular distributions	112
	From energy distributions of detached electrons	114
	Measurement of optical excitation functions	114
4.8	Experimental study of autodetaching states through photodetachment	115
4.9	Doubly excited states which decay through emission of radiation – change of parity	115

CHAPTER 5

Autodetaching states of specific atomic negative ions

5.1	H ⁻	116
	The (2p) ² 3P _e state	120
5.2	He ⁻	122
	He ⁻ states below the excitation threshold (19.8 eV)	122
	The 1s2s ² 2S state	122
	The 1s2s2p ⁴ P state	126
	States between the excitation and ionization thresholds – 2 ² P and 2 ² D	135
	Triply-excited states of He ⁻	138
5.3	Negative ions of heavier rare gases	142
5.4	O ⁻	143
5.5	N ⁻	144
5.6	Cl ⁻	146
5.7	Negative ions of the alkali metal atoms	148
5.8	Doubly-charged negative ions	150
	H ²⁻	151
	Other doubly-charged negative ions	151

CHAPTER 6

Molecular negative ions – ground states

6.1	The quantum states of diatomic molecules – potential-energy curves	156
-----	--	-----

6.2	Enumeration and properties of the electronic states of diatomic molecules	page 160
6.3	The vibrational and rotational energy	162
6.4	The Franck-Condon principle	165
	Electron affinity and vertical detachment energy	166
6.5	Theoretical calculation of the properties of the ground states of diatomic molecules	166
6.6	The observation of autodetaching levels associated with the ground states of diatomic negative ions	168
6.7	Electron affinities of diatomic molecules and structure of the ground states of the negative ions	172
	The determination of electron affinities of diatomic molecules	172
	Determination of structural properties of diatomic molecular ions	174
	H_2^-	174
	OH^- and SH^-	179
	Other diatomic hydrides	183
	O_2^-	183
	SO^- and S_2^-	190
	NO^-	191
	N_2^-	194
	CO^-	204
	C_2^-	207
	CN^-	210
	F_2^- , Cl_2^- , Br_2^- , I_2^-	210
	Other diatomic molecules	213
6.8	Polyatomic negative ions	214
	O_3^-	215
	SO_2^-	215
	NO_2^-	216
	N_2O^- and CO_2^-	218
	NH_2^- , PH_2^- , AsH_2^-	218
	NO_3^-	219
	O_4^-	220
	CO_3^- and CO_4^-	220
	SF_6^- and TF_6^-	221

CHAPTER 7

Excited electronic states of molecular negative ions

7.1	Introduction	<i>page</i> 222
7.2	H_2^-	222
7.3	N_2^-	228
7.4	CO^-	235
7.5	O_2^-	237
7.6	NO^-	237

CHAPTER 8

Modes of formation of negative ions – formation by radiative processes – radiative attachment and polar photodissociation

8.1	Radiative capture of electrons – electron affinity spectrum	242
8.2	Direct observation of affinity spectra	248
	Experimental methods	248
	Observed results	252
8.3	Dielectronic attachment	254
8.4	Polar photodissociation	255

CHAPTER 9

Modes of formation of negative ions – formation by three-body collisions and by collisions of electrons with molecules – dissociative attachment and polar dissociation

9.1	Capture of electrons in three-body collisions	264
9.2	Formation of negative ions on collisions of electrons with molecules – theoretical introduction	266
	Processes involving electron capture	266
	Non-capture collisions – dissociation into ions	272
9.3	Formation of negative ions on collision of electrons with molecules – experimental methods of study using homogeneous electron beams	274
	Introductory remarks – early techniques	274
	Measurement of total attachment cross-sections	278
	Measurement of the velocity distribution and composition of the ions	282
	Measurements employing mass analysis but not energy analysis	284

	Measurement of the angular distribution of the ionic momenta	<i>page</i> 288
9.4	Formation of negative ions in collision of electrons with molecules – attachment experiments with electron swarms	290
	Introductory remarks	290
	General description and theory of swarm experiments	291
	Experimental methods	292
9.5	Discussion of results of experiments on attachment of electrons to diatomic molecules	309
	H ₂ , HD and D ₂	309
	O ₂	316
	CO	333
	NO	338
	Halogen molecules	341
9.6	Attachment to polyatomic molecules	345
	H ₂ O	347
	NH ₃	351
	CO ₂	352
	N ₂ O	358
	NO ₂	365
	O ₃	366
	SF ₆	368
	Other halogen-containing molecules	376

CHAPTER 10

	Formation of negative ions by capture of bound electrons	
10.1	Formation of negative ions in collisions between neutral systems	383
10.2	Low-energy experiments on the measurement of cross-sections and threshold energies	389
	Some typical experimental arrangements	391
	Results obtained in low-energy experiments	394
10.3	High-energy experiments – experimental methods	399
	Electron capture by H atoms	399
	Production of He ⁻	405
10.4	Negative-ion formation by double capture of electrons	414

CHAPTER II

Detachment of electrons from negative ions – photodetachment, field detachment and detachment by electron impact	
II.1	Introduction page 416
II.2	Photodetachment – introductory theoretical considerations 417
II.3	Calculated photodetachment cross-sections 421
	H ⁻ 421
	Other atomic negative ions 424
II.4	Photodetachment – experimental methods 430
	Introduction 430
	Crossed-beam methods 432
	Measurement of the energy and angular distribution of the detached electrons 438
	Absorption by shock-heated alkali halides 442
	Photodetachment studies using an ion cyclotron resonance spectrometer 445
	Photodetachment from ions aged in a drift tube 448
II.5	Application to different atomic negative ions 449
	H ⁻ 449
	He ⁻ 450
	O ⁻ 450
	S ⁻ and Se ⁻ 454
	C ⁻ 458
	Halogen negative ions 459
	Negative ions of the noble metals 461
	Negative ions of the alkali metal atoms 466
	Other atomic ions 472
II.6	Application to different molecular negative ions 473
	OH ⁻ , OD ⁻ and SH ⁻ 473
	CH ⁻ 477
	NH ⁻ 478
	O ₂ ⁻ 478
	NO ⁻ 482
	C ₂ ⁻ 484
	S ₂ ⁻ 484
	SO ⁻ 484
	NH ₂ ⁻ , PH ₂ ⁻ , AsH ₂ ⁻ 486

	SO_2^-	<i>page</i> 487
	NO_2^-	488
	Other negative ions of atmospheric interest	489
11.7	Multiphoton detachment	489
11.8	Detachment from negative ions in electrostatic fields	495
	Theoretical considerations	495
	The measurement of the rate of field detachment from H^-	497
	Field detachment from excited negative ions	500
11.9	Detachment by electron impact	500
	Theoretical considerations	500
	Measurement of detachment cross-sections	503
	Results obtained for single detachment	509
	Double detachment	512

CHAPTER 12

Detachment, charge transfer and other reactions between negative ions and neutral systems at low and intermediate energies

12.1	Classification of types of ionic reaction	513
12.2	Orbiting collisions	514
12.3	The theory of detachment reactions	516
12.4	Ionic mobilities	519
12.5	Experimental methods for measuring mobilities and/or reaction rates for negative ions in gases	521
	The combined drift-tube and mass-spectrometer technique	522
	The flowing afterglow method	526
	Experiments in static afterglows	528
	Extension of the pulse method	530
	Experiments with low-energy ion beams	534
12.6	The determination of threshold energies for endothermic charge transfer reactions	537
12.7	Discussion of observed results	540
	Mobilities and reactions of oxygen ions in oxygen	540
	Reactions of oxygen negative ions with atoms and molecules of other species	549
	Reactions of negative ions other than those of oxygen	560

CHAPTER 13

Detachment, charge transfer and other reactions involving negative ions – collisions at high impact energies

13.1	Symmetrical charge transfer – theoretical considerations	<i>page</i> 579
	Effect of detachment on charge transfer cross-sections	584
13.2	Unsymmetrical charge transfer – theoretical considerations	586
13.3	Calculation of detachment cross-sections	587
13.4	The measurement of charge transfer and detachment cross-sections	590
	The condenser plate method	591
	Crossed-beam method	597
13.5	Observed results	599
	H ⁻ -H collisions	599
	Charge transfer reactions involving atomic negative ions and neutral atoms	602
	Charge transfer reactions involving molecules	603
	Detachment reactions involving H ⁻ ions and other neutral species	605
	Detachment from He ⁻	610
	Detachment reactions involving other negative ions	612
	Double detachment	614

CHAPTER 14

Recombination of negative and positive ions – mutual neutralization

14.1	Theoretical considerations	618
	Mutual neutralization	618
	Recombination in three-body collisions	621
14.2	The measurement of recombination and mutual-neutralization rates	625
	The medium pressure range	625
	Measurements at high pressures	628
	Measurements at low pressures – rate of mutual neutralization	628

	Measurements by merging and inclined-beam techniques	<i>page</i> 632
14.3	Results obtained for specific mutual-neutralization reactions	635
	H^+-H^-	635
	N^+-O^- , $N_2^+-O_2^-$, $O_2^+-O_2^-$	638
	He^+-H^-	639

CHAPTER 15

Negative ions in electric discharges, planetary and stellar atmospheres, trace analysis and tandem accelerators

15.1	Negative ions in glow discharges	640
	General effects of negative ions in discharges	640
	Analysis of a discharge in oxygen	642
15.2	The effect of negative ions on current build-up and electrical breakdown in gases	653
	Current build-up and breakdown in air and oxygen	657
	Current build-up and breakdown in halogen-containing substances	660
15.3	Negative ions in the terrestrial ionosphere	663
	Introduction	663
	The lower ionosphere	666
15.4	Negative ions in the atmospheres of the sun and stars	673
	H^- and the continuous emission spectrum of the sun	673
	The emission spectrum in terms of atmospheric absorption coefficients	673
	The contribution from free-free absorption	680
	Negative ions in stellar atmospheres	682
15.5	The application of electron attachment to the qualitative and quantitative analysis of trace samples – the electron capture detector	682
15.6	The use of negative ions in particle accelerators	690
	Tandem accelerators	690
	H^- ions in cyclotrons and synchrocyclotrons	691
	<i>References</i>	693
	<i>Author index</i>	717
	<i>Subject index</i>	727