

Index

- Actin 194
S-adenosylmethionine 194–5
Adenosine triphosphate (ATP) 172, 190, 194
Alanylhistidine 29, 30
Alanylserine 28, 29
Albumin 34, 169–70, 190, 191
Alcohols/alcoholates 25, 40, 41
Aldaric acids 33
Alkoxides 64, 65
Alkylation and alkylating agents 177–8
Amanita muscaria 100
Amanita spp. 37, 81, 100, 205
 X-ray studies 84
Amavadin 21, 37, 39, 81, 100–5, 205
 in *Amanita muscaria* 102–3
 in *Amanita* spp. 100
 catalytic actions 103
 characteristics 100–1
 hydroxamido complexes 104–5
 ligands
 noninnocent 59, 60
 stabilising 103–4
 non-oxo complexes 103–4
 structure 100–2
 X-ray studies 84
Amoebiasis (amoebic dysentery) 179–80
Anhydrides 189–90
Aqueous vanadium systems 13–26
 aqua-sulfato complexes 15
 and pH 15, 16, 19
 predominance diagrams 17
 protonation/deprotonation 18, 19
 speciation/speciation diagrams 16–17
 vanadate structures 17–18
Archaea 146, 205
Aryl sulfatases 197
Ascidians 9–10, 15, 67, 74, 87–96
 anatomy 87
 blood 88–9, 90
 glutathione transferases (GST) 96
 habitat and life style 88
 K-edge X-ray absorption spectroscopy
 92, 93
 and oxygen 88–9
 signet ring cells (vanadocytes) 67, 89, 90–1
 sulfur compounds 92, 94
 tunichromes 91
 vanabins 93, 94–6
 vanadium
 in blood 90
 composition 91, 92
 concentration 88
 discovered 87
 entry into organism 93
 redox chemistry 93–4
 and water ligands 91–2
 XAS studies 84
Ascophyllum nodosum 84, 107, 109–10, 111,
 113, 114
Asimov, Isaac 203, 204, 205
Azotobacter spp. 84, 128, 129, 131, 149–50
Bacterial action 5–6, 128, 129–30, 145–50
Baes–Mesmer diagram 13, 14
Berzelius, J. J. 1, 2, 4, 8
Binary vanadium(IV and V) systems 20–4
Biological importance of vanadium 9–10, 205
 in bones 170–1
 and cellular functions 157–98
 metabolic pathways 157–8
 reaction paths 172, 173

- Biological importance of vanadium
(Continued)
effect on animals 8, 9
in human body 5, 9, 157
spectroscopic investigations 83–4
spemicidal activity 180–1
- Blood 26–8, 190–1
see also Plasma; Serum components
- BMOV 169
- Bones 20, 170–1
- Bortels, Hans 128
- Bromoform 108
- Bromoperoxidases 107–8, 109, 111
- Cancer therapy 176–9
cancer types 176
and DNA 177, 179
tyrosine phosphatase inhibition 176–7
- Carboxylates/carboxylato 27, 42, 43, 142
- Catalytic action
by amavadin 103
in haloperoxidases 116–17
by peroxovanadium complexes 121
of vanadium oxides 7, 8
of vanadium-phosphate salts 21
- Catechols/catecholates/catecholato 41, 42, 91,
97–8, 142
- Cellular functions 157–98
- Chemistry, contribution to humanity 203
- Chloroperoxidases 107–8, 111
- Chromium 1, 2, 4
- Circular dichroism (CD) 79–80
applications 79, 80
magnetic circular dichroism 79
- Cisplatin 178
- Citric acid and derivatives 26, 27, 28, 33–4,
73, 143, 168
- Clostridium butyricum* 129
- Coordination compounds of vanadium 34–47
- Copper zinc superoxide dismutase
(CuZn-SOD) 193–4
- Corallina spp.* 107, 110, 111, 113
- Curvularia inaequalis* 107, 109–10,
111, 113
- Cyclopentadienylvanadium complexes
47, 180
- Cysteine 32, 45, 94, 103, 186, 196–7
- Decavanadate 18, 19, 34, 194, 195, 196
- Del Rio, Andres Manuel 3–4
- Diabetes mellitus 158–63
control 159
- and glucose metabolism/uptake 158, 166
and insulin 158, 159, 160, 172–5
insulin receptor substrates (IRS) 174–5
treatment 159–60
Type 1 and Type 2 159
- vanadium compound treatment 160–5
chronology 162–3
insulin-mimetic action 161, 164–5, 166,
175, 186
- organovanadium compounds 162–5
activity levels 163–5
advantages 162
ligands 163
oxidation state 163
peroxovanadate 161–2
serum interaction 165–7
vanadium absorption 169
vanadyl sulfate 161
- Dithiolene 44, 45
- Dithiothreitol 30, 31
- Divanadate 19
- DNA cleavage 179
- DNA damage
alkylation 177–9
agents 177–8
dealkylation 178
oxidative 177
- Ehrlich tumours 178, 179
- Electron absorption spectroscopy 21–2
- Electron nuclear double resonance
spectroscopy, see ENDOR spectroscopy
- Electron paramagnetic resonance (EPR)
spectroscopy 21–2, 31–2, 53, 67–75
anisotropic axial spectra 68–9
applications 69–74
complex distortions 71–2
dinuclear complexes 73, 74
equatorial ligand set
assignment 69–70
size 70–1
superoxo complex formation 74–5
valence localisation 73
vanadium complex parameters 71–3
compared with NMR 67
haloperoxidases 113
hyperfine coupling constants 69–70
resonance conditions 68
spin criteria 67–8
on vanadium nitrogenases 134
- Electron spin-echo envelope modulation
spectroscopy, see ESEEM spectroscopy

- ENDOR spectroscopy 75, 76–7
 electron spin echo ENDOR (ESE-ENDOR)
 77
 procedure 76
Entamoeba histolytica 179–80
Enterobactin 149
Enzymes 121–5
ESEEM spectroscopy 75–6, 113, 170
 procedure 75–6
Esters 26, 36, 189–90, 191
 MAS spectra 64, 65
 of orthovanadic acid 25, 26, 41, 59
 sulfate ester hydrolysis 197–8
- Ferrovandium 8
Fly agaric 100
Fossil ‘fuels’ 6–7
 crude oil 6, 7
- Geobacter metallireducens* 149
Glucose-6-phosphatase 187
Glutathione (GSH) 30–1, 172, 173
Glutathione transferases (GST) 96
Glycyl-L-cysteine 32
Glycyl-L-histidine 32
Groundwater 149
- Haber–Bosch process 130
Haemovanadin 89–90
Halides
 of orthovanadic acid 24–5
 in sea water 107–8
Haloperoxidases, *see* Vanadate-dependent
 haloperoxidases (VHPOs)
Apo-haloperoxidases (apo-VCIPO) 109,
 187–8
Health risks 7–8
 concentration levels 8
Henze, M. 9–10, 87, 88, 89, 90
Histidine
 complexes 29, 30, 32, 121–2
 in phosphatases 186, 187
HIV 180–1
Homocitrate 131–3, 143
Humboldt, Baron von 1
Hydrazine 134, 138, 141–2
Hydrogen bonding 195–6
Hydrogencarbonate 20
Hydrogenphosphate 20
Hydroxamido groups/ligands 59, 104–5
Hydroxycarboxylates 27
Hydroxylamine 21, 23–4
- Imidazole 30, 32, 70–1
Insulin 158, 159, 160
 binding modes 194
 and maltolovanadium 22
 stimulates glucose uptake 172–5
 vanadium as mimetic agent 161, 164–5,
 166, 175, 186
Insulin receptor substrates (IRS) 174–5
Iodoperoxidases 107–8
Iron mobilisation 149
- Johnston, J. F. W. 2, 4
- Keggin structure 19–20, 22
Kinases 146, 175
- Lactamases 189
Lactic acid and lactate 26–7, 33
Lactoferrin 192, 193
Laws of Robotics 203, 205
Ligands
 sulfate 15, 27, 90–93, 98–100
 thiofunctional 30, 43–5
 vanadate/vanadyl interactions 26–34
Lipolysis 175
Lippmann, E. O. von 9
Lysosomal storage diseases 197
- Magnetic circular dichroism (MCD) 79
Maltol 162, 167, 172, 173
Maltolovanadium 22
Medicinal aspects of vanadium 9,
 158–82
Metabolic pathways 157–8
Metavanadates 20
Metronidazole 180
‘Metvan’ 176
Molybdenum, in nitrogen cycle 128–9
Molybdenum nitrogenase 131, 134
Molybdopterines 144, 145
Monovanadate 19
Myosin 194
- Nitrate reductases 144–5
Nitrogen cycle 128–45
 bacterial action 128, 129–30
 chemical steps 129–30
 historical aspects 128–30
 molybdenum (role of) 128–9
 tungsten (role of) 128, 129
 vanadium (role of) 128–9, 130
 vanadium nitrogenase 131–44

- Non-oxo vanadium complexes 35, 41, 45
- Nuclear magnetic resonance (NMR) 66–7
 coordination-induced shift (CIS) 66
 paramagnetic vanadium(III) 67
see also Vanadium-51 NMR spectroscopy
- Optical spectroscopies 77–80
- Organovanadium compounds (organic vanadium compounds) 47–8
 diabetes treatment 162–5
see also Vanadium-carbon bond
- Orthovanadates 20
- Orthovanadic acid
 esters 25
 structure 25, 26
 halides and other salts 24–5
- Oxidation reactions
 haloperoxidase reactions 116–18, 121, 124, 125
 of sulfides 114
 superoxo intermediates 167–8
- Oxidation states 13–15, 48, 163
- Oxovanadium complexes 31, 35, 167–8
 ROS scavengers/generators 177
- Pentavanadate 19
- Peroxidases
 classification 105
 historical background 105–6
 isolation 106
see also Vanadate-dependent haloperoxidases (VHPOs)
- Peroxides 20–1, 22, 27, 30
- Peroxo ligands 37, 38, 59
- Peroxovanadates 20–1, 24, 186
- Peroxovanadium complexes 116–17, 119–21
 catalytic action 121
 coordination numbers 120
 oxidation reactions 121
 speciation 120–1
 structure 119–20
- Phallusia mamillata*, *see* Ascidians
- Phosphatases 30, 109, 175, 183–4, 187–8
 structure 186
- Phosphate-metabolising enzymes 183–9
 inhibited by vanadate 184–8
 phosphatases 184, 186–8
 ribonucleases 184–6
 stimulated by vanadate 189
- Phosphate–vanadate antagonism/competition 20, 25, 182, 183, 193–4
- Phosphates 20, 21, 26, 27
- Phosphovanadates 24, 190–1
- Phytic acid and phytases 188
- Picolinato ligand 169
- Plants 9
- Plasma 5, 20, 190–1
see also Blood; Serum components
- Pollution 7
- Polychaeta fan worms 96–7
 vanadium
 accumulation 96–7
 function 97
- Polyoxometalates (POMs) 181
- Porphingens 7
- Priestley, John 9
- Protein tyrosine phosphate (PTP) 174–5, 182, 186–7
- Proteins 182–98
 bind to vanadate 182, 190–5
 bind to vanadyl 94–5, 182, 190–5
 in blood plasma 190–1
 modified by vanadate 195–8
 nonfunctional binding of vanadate and vanadyl 190–5
 occurrence 182
 in vanadium nitrogenase 131–3
- Pseudopotamilla ocellata*, *see* Polychaeta fan worms
- Pyridinone complex 171
- Quinta essentia* 203–4
- Radioactivity 5
- Redox potentials 13, 14, 15
- Respiration 146
 electron acceptors 146
 vanadate as substrate 146
- Ribonucleases (RNases) 184–6
 vanadate incorporation 184–6
- Roscoe, Henry Enfield (Sir) 4
- Schiff base complexes 45, 46–7
- Sea squirts, *see* Ascidians
- Sea water 5, 107–8, 145
- Sefström, Nils Gabriel 2
- Serine 28–30, 126–7, 149, 195–6
 photocleavage 195–6
 reaction steps 196
- Serum components 165–7
 albumin 169–70, 190, 191
 proteins 190
 transferrin (Tf) 34, 168, 169–70, 171–2, 190–1, 193

- water 167
 - as ligand 167
 - see also Blood; Plasma
- Sherwoodite 5–6, 146
- Shewanella oneidensis* 146–7
- Siderophores 149, 150
- Signet ring cells 20, 25, 182, 183, 193–4
- Speciation analysis, notation 31
- Spectroscopic methods 53–84
- Spermicidal properties 180–1
- Sulfatases 196, 197
- Sulfate ester hydrolysis 197–8
- Sulfatovanadium complexes 98–9
- Sulfhydrases 196–7
- Sulfides 43, 109
 - oxygenation 124, 125
 - peroxidation 124–5
- Ternary vanadium(IV and V) systems 20–4
- Tetравanadate 19, 194, 195
- Thioacetals 124, 125
- Thiocyanates 108–9
- Thiofunctional ligands 30, 43–5
- Thiol (mercapto) groups 30–1
- Thiovanadates 20
- Transferrin (Tf) 34, 168, 169–70, 171–2, 190–1, 193
- Tridecavanadate 19–20
- Tuberculosis 181–2
- Tunicata/tunicates 87, 88, 146
- Tunichromes 41, 74, 91, 97–8
- Two-dimensional exchange spectroscopy (2D-EXSY) 60–1
- Ultra-violet spectroscopy, see UV-Vis spectroscopy
- Uranium 2
- UV-Vis spectroscopy 77–9
 - conditions 77
 - vanadium(III) complexes 79
 - vanadium(IV) complexes 78
 - vanadium(V) complexes 77–8
- Vanabins 93, 94–6, 182
 - amino acid sequences 95
 - binding functions 96
 - structure 95
- Vanadate
 - dealkylating action 178
 - decavanadate 18, 19, 34, 194, 195, 196
 - divanadate 19
 - electron acceptor 145–50
 - in groundwater 149
 - inhibitory effect 184–5
 - monovanadate 19
 - pentavanadate 19
 - phosphate compared 182, 183
 - protein binding 182, 190–5
 - competes with phosphate 20, 193–4
 - nonfunctional 190–5
 - site nature 191–3
 - spectroscopic analysis 192–4
 - proteins, modification 195–8
 - in *Shewanella oneidensis* 146–7
 - electron transfer pathway 147, 148
 - location 147, 148
 - TEM images 147, 148
 - as stimulant
 - of glucose uptake 172–5
 - and lipolysis 175
 - phosphorylation 174–5
 - of phosphatase activity 189
 - structures 17–18
 - system speciation 26–31
 - tetравanadate 19, 194, 195
- Vanadate–alanylhistidine system 30, 121–2
- Vanadate–alanylhistidine–peroxide system 30, 121–2
- Vanadate–alanylserine system 28–30
- Vanadate-dependent haloperoxidases (VHPOs) 105–28, 182, 183, 186
 - activity data 109–10
 - bonding
 - carbon–hydrogen bonds 128
 - hydrogen bonding 126–7
 - bond lengths 127
 - and water 127–8
 - of vanadate centre 125–6
 - distribution 105, 107
 - halides
 - converted to hypohalous acid 107–8, 114–15
 - oxidation (active species) 113
 - inhibition 109
 - isolation 106
 - model chemistry 116–28
 - enzymes 121–5
 - functional models 118, 123
 - halogenation 123
 - hydroxylation reactions 117–18
 - monobromination catalysis 117
 - organic syntheses 123

- Vanadate-dependent haloperoxidases (VHPOs)
(*Continued*)
- oxidation reactions 117–18
 - sulfides/thioacetals reactions 124
 - oxo transfer reactions 116
 - peroxovanadium complexes 116–17
 - structural models 118, 119–21
 - peroxovanadium complexes 119–21
 - reduced haloperoxidases 119
 - peroxo/hydroperoxo intermediates 115, 117
 - protonation 114–15
 - structure 110–16, 186
 - active sites 111, 112
 - bonding and bond lengths 111–12
 - EPR linewidths 113
 - helices 110, 111
 - MAS spectra 114
 - reduced form 112–13
 - X-ray diffraction data 112, 113–14
 - substrates 107–9
 - sulfides 115–16
 - uses 109
 - and vanadate-inhibited phosphatases 186, 187–8
- Vanadate-dependent peroxidases, *see*
Vanadate-dependent haloperoxidases (VHPOs)
- Vanadate-inhibited phosphatases 187–8
- Vanadate–hydroxylamine system 23–4
- Vanadate–peroxide system 22, 23
- Vanadate–phosphate antagonism/competition 20, 25, 182, 183, 190–1, 193–4
- Vanadate–phosphate–peroxide system 22–3
- Vanadate–phosphate system 21–2
- Vanadinite 2, 3
- Vanadium
- discovery 1–5
 - inorganic compounds 13–48
 - isolation 4
 - minerals 5–6
 - naming 2
 - occurrence 5–6, 145
 - radioactivity 5
 - redox chemistry 93–4
 - synthesis 4–5
- Vanadium-51 NMR spectroscopy 16, 53–66
- criteria 53
 - linewidths 61–2
 - influential factors 62
 - molecular correlation time 62
 - quadrupole coupling constant 62
 - relaxation process 61–2
 - nuclear spin–spin coupling 62–3
 - Fermi contact term 62–3
 - relaxation effects 63
 - parameters under ‘confined’ conditions 64–6
 - magic angle spinning (MAS) 64, 65
 - magnetic field strength 66
 - quadrupolar interactions 64
 - Zeeman transitions 64
 - quadrupolar nuclei 53, 54
 - reference standard 54
 - scalar coupling 62–3
 - shielding ranges 57–60
 - coordination geometry 58–9
 - coordination number 58–9
 - electronegativity dependence 57–8
 - noninnocent ligands 59–60
 - peroxo and hydroxamido ligands 59
 - shift limits 57
 - steric effects 59
 - theory 55–7
 - LCAO coefficient 56
 - molecular orbital scheme 56–7
 - paramagnetic term 56
 - shielding 54, 55–6
 - vanadium nucleus parameters 53–4
- Vanadium–carbon bond 47–8
- bonding interaction 48
 - occurrence 47
 - oxidation states of vanadium 48
- Vanadium coordination compounds 34–47
- and biogenic ligands 40–7
 - alcohols and alcoholates 40, 41
 - carboxylates/carboxylato 42, 43
 - catecholates/catecholato 41, 42
 - enolates/enolato 41, 42
 - mixed ligand spheres 46–7
 - multifunctional ligands 45–6
 - phenolates/phenolato 41, 42
 - thiofunctional ligands 43–5
 - structural features 34–9
 - bond lengths and bond orders 36–7
 - bridging ligands 37–8
 - chelating ligands 39
 - chirality 39
 - coordination geometries 37
 - octahedral arrangement 36, 37
 - oxo- and dioxovanadium complexes 35
 - peroxo ligands 37, 38
 - substitution variations 38

- trans* influence 36
 - vanadium–carbon bond 47–8
 - vanadium–oxygen bond 36–7
- Vanadium lead ore 2
- Vanadium-metabolising enzymes 183–8
- Vanadium nitrogenase 131–44, 182, 204–5
 - cluster structure 131–2
 - M** clusters (iron–vanadium cofactor, FeVco) 131, 132, 134, 143
 - P** clusters 131, 132, 134
 - constituents 131
 - model chemistry 135–44
 - alkyne coordination 143–4
 - catecholato complexes 142
 - citrate coordination 143
 - cubane clusters 142–3
 - dicarboxylates 142
 - dinitrogen activation/reduction site 135–6
 - dinitrogen-bridged complexes 139–41
 - dinitrogen vanadium complexes 138–9
 - hydrazine reactions 138
 - metal centre 135–6
 - nitrogen–nitrogen bond 139–41
 - phosphine 138–9
 - vanadium–nitrogen bond 140–1
 - Yandulov–Schrock cycle 136, 137
 - molybdenum nitrogenase compared 131, 134
 - protein components 131–3
 - reduction reactions 131, 134–5
 - in alkaline solutions 141–2
 - of azide 135
 - hydrocarbon substrates 134–5, 143–4
 - of methyl isocyanide 135
 - structure information
 - from EPR spectra 134
 - from XAS investigations 133–4
 - VFe-protein 131–3
 - biosynthesis 132–3
- Vanadium oxides 7, 8
 - catalytic action 7, 8
 - physiological importance 13–15
 - reduction 13–15
- Vanadocene dichloride 176, 178–9
- Vanadocenes 178
- Vanadocytes 67, 89, 90–1
- ‘Vanadophores’ 149, 150
- Vanadyl 16
 - complexes 167–8
 - coordinates with ATP 190
 - as phosphate analogue 182
 - protein binding 182, 190–5
 - nonfunctional 190–5
 - physico-chemical marker 194
 - site nature 191–3
 - spectroscopic analysis 192–4
 - system speciation 31–4
- Vanadyl–ligand A–ligand B system 168–9
- Vanadyl–phosphate complexes 21–2
- Vanadyl–picolinate–phosphate/citrate complexes 171–2
- Vilter, Hans 106
- Westinghouse Lamp Co. 4–5
- Wine 204
- Wöhler, F. 1, 2, 8
- X-ray absorption spectroscopy (XAS) 80–4
 - biological applications 83–4, 92–3, 107, 112, 133
 - extended X-ray absorption spectroscopy (EXAFS) 80, 81, 82, 133–4
 - K-edge 80–2, 92, 93
 - L-edge 83
 - near-edge X-ray absorption fine structure (NEXAFS) 80
 - pre-edge 81–2
 - on vanadium nitrogenase 133–4
 - X-ray absorption near-edge structure (XANES) 80–3
- Xylose isomerase 195
- Yandulov–Schrock cycle 136, 137

