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J.H.L. Voncken

The Rare Earth Elements

An Introduction



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Preface

This book was written as a summary of my long-standing interest in rare earth elements, which had started already when I was a master student at Utrecht University in the 1980s. Having begun seriously to tackle the topic early in 2009, it appeared that, during the so-called rare earth crisis from 2009 to approximately 2013, I was considered a kind of ‘sole expert’ in the Netherlands on rare earth element resources. This led me to being asked to give numerous presentations.

As a result of these many presentations, I realised that there was little or no information on the rare earth elements for the well-educated non-expert. So, in June 2014, after having given the umpteenth presentation on rare earth elements for an audience of members of the Groningen Department of the Royal Dutch Chemical Society (KNCV), I started with the preparations for writing this book.

This book is thus intended for the well-educated but non-expert reader, from any natural science discipline. This also explains the numerous footnotes scattered throughout the book, which are intended to elucidate the used terminology, or to supply short background information.

For the opportunity to write this book, I first of all would like to thank Dr. Mike Buxton, Head of the Resource Engineering Section, Delft University of Technology, who earnestly suggested me to write this work and allowed me to write it as part of my duties at Delft University. He also mentioned the importance of the South African Pilanesberg and Steenkampskraal deposits and supplied me with several papers and reports from the literature on these and other deposits.

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Delft
October 2015

Jack Voncken

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Chapter 1

The Rare Earth Elements—A Special Group of Metals

Abstract This chapter explains what the rare earth elements are, where and when they were discovered, and by whom. The name of each element is explained (as the elemental names are rather exotic), the misleading name for these metals, which suggests that they are rare (which they are not), is clarified, and the fact that they are not earth metals is established. The alkaline earth metals constitute group IIA in the periodic system, consisting of Be, Mg, Ca, Sr, Ba, and Ra; the rare earth elements are transition metals (group IIIB).

1.1 Introduction

Over the last few years, more and more people have become aware of a rather special group of metals: the rare earth elements. Many people have never heard of them, or probably just know them as “the upper one of these two rows of elements beneath the main body of the Periodic System of the Elements”. Indeed, these metals, with a surprisingly large amount of applications, were rather obscure to the general public until 2009.

In 2009, China, which had almost a monopoly on the production of these elements (97 % of the world production), changed its position towards the world-wide rare earth market. China introduced production quotas, export quotas and export taxes, enforced environmental legislation, and granted no new rare earth mining licenses (Geschneider 2011). This caused world-wide anxiety among manufacturers of high tech equipment, because many of today’s common (mostly) high-tech applications are not feasible without rare earth elements. Notable examples are hard-disk drives, smart phones, flat-screen televisions and monitors, rechargeable batteries (household and automotive) and tiny earphones. Others are lasers, strong permanent magnets for electrical generators, glass-polishing powders, and energy-saving lamps. This period, starting in 2009 and known as the “Rare Earth Crisis,” made many people around the world aware of this peculiar group of elements.

Mendeleev's Periodic Table of Elements

Table of Common Polyatomic Ions

Element categories

State of matter at 25 °C

Gas Liquid Solid Artificially prepared Unknown

1 1A 2 1A 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 18 18A

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 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528 529 530 531 532 533 534 535 536 537 538 539 540 541 542 543 544 545 546 547 548 549 550 551 552 553 554 555 556 557 558 559 560 561 562 563 564 565 566 567 568 569 570 571 572 573 574 575 576 577 578 579 580 581 582 583 584 585 586 587 588 589 590 591 592 593 594 595 596 597 598 599 600 601 602 603 604 605 606 607 608 609 610 611 612 613 614 615 616 617 618 619 620 621 622 623 624 625 626 627 628 629 630 631 632 633 634 635 636 637 638 639 640 641 642 643 644 645 646 647 648 649 650 651 652 653 654 655 656 657 658 659 660 661 662 663 664 665 666 667 668 669 670 671 672 673 674 675 676 677 678 679 680 681 682 683 684 685 686 687 688 689 690 691 692 693 694 695 696 697 698 699 700 701 702 703 704 705 706 707 708 709 710 711 712 713 714 715 716 717 718 719 720 721 722 723 724 725 726 727 728 729 730 731 732 733 734 735 736 737 738 739 740 741 742 743 744 745 746 747 748 749 750 751 752 753 754 755 756 757 758 759 760 761 762 763 764 765 766 767 768 769 770 771 772 773 774 775 776 777 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Fig. 1.2 Johann Gadolin.*Image Source* Wikipedia

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Reference Dean and Dean

(1996)



1.2 Atomic Structure

In the lanthanides (the elements La–Lu) the *f-orbitals*, which have 7 sub-orbitals, are filled. Each suborbital holds two electrons. As a result of this, there are 15 possibilities for filling the *f-orbitals*, giving rise to 15 lanthanide elements. These elements have closely related properties.

The lanthanides are all trivalent (3+), with the exception of cerium (which also forms 4+ ions), and europium, ytterbium, and samarium, which also will form 2+ ions.

The elements scandium and yttrium, which are also considered to belong to the rare earth elements (because of their similar chemical behaviour) also have a 3+ oxidation state. The atomic structure of the REE is further discussed in Chap. 3 (Physical and Chemical Properties of the Rare Earths).

1.3 Radioactivity

Of the rare earth elements, only one element is radioactive and has no stable isotopes. All other of these elements have stable isotopes, although for several elements, the isotopes have limited stability, but a very long half-life, so they may be considered stable. The radioactive element without a stable isotope is the element promethium (Pm). Promethium does not occur as a free element on Earth, whether as a metal or in compounds. It is synthetically manufactured in nuclear reactors, as it has practical applications. The radioactivity of promethium is further explained in Chap. 3.