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Introductory Chapter: Chalcogen Chemistry - The Footprint into New Materials Development

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1. Chalcogen chemistry – the footprint into new materials development

The study of chalcogen chemistry is just fascinating for two reasons. Firstly, they span the entire biotic communities connecting chemistry to many other scientific disciplines. These include biogeochemistry, biochemistry, biology, food, agriculture, and also medicine, as well as pharmacology. Secondly, the chalcogen elements known as chalcogens demonstrate extremely interesting properties forming new compounds endowed with sophisticated characteristics that are increasingly making a remarkable footprint in a new era of materials development. These two reasons have intensified worldwide exploration of chalcogen elements contained in natural compounds as minerals. Furthermore, the aforementioned reasons have motivated research focused on expanding knowledge on this special class of compounds. In the past few decades, the shift of interest has been toward the development of new materials (in combination with metals and ligands). The contribution of this field of chemistry to the development of new materials, and their impacts on the everyday life of mankind, has triggered a recent renaissance of the interconnectivity between new chemical concepts and reactivities, resulting in a multitude of multidisciplinary focused research niche areas. The unique structures and reactivity of the class of chalcogen compounds and materials [1, 2] as well as their fascinating optical [3, 4] and electronic properties [5, 6] confer onto them very wide potential applications [7–12].

Group 16 or group VI-(A) elements in the modern periodic table comprising of oxygen (O), sulfur (S), selenium (Se), tellurium (Te), and polonium (Po) are usually called chalcogens (“ore builders”) [13, 14]. The most valuable fundamental characteristic of these elements is their versatile nature to form new bonds and new compounds [15–17]. In this regard and

with respect to the periodic law, the properties of the chemical elements in the chalcogen group are not arbitrary, but depend upon the structure of the atom and vary with the atomic number in a systematic way [13, 14]. In a geochemical sense, the chalcogens are referred to as soft elements, thus, also named chalcophiles [18, 19].

Geometrically, chalcophiles are the soft elements (one must keep in mind the terminology of the hard/soft acids and bases concept) [13, 20]. The modern term “chalcogen” is a derivation of two Greek words *chalcos* or “*khalkós*,” meaning “ore formers” [19]. This word also means copper (and had also been used for bronze/brass or coin during the ancient time). One valid reason is that they are found in copper ores. The second word is a latinized Greek word “*genēs*” (meaning born or produced). These two words gave birth to the coined term “*khalkos-genes*” or to today’s modern term chalcogens [21, 22]. Earlier on, chalcophiles were thought to be electron rich [13]. They are described as the low-valent elements of the Group 16 elements (O, S, Se, Te, and Po) or particularly electronegative elements and often bond to the functional groups of organic molecules [13] and/or are found as electron donors for the transition metals [23, 24]. This property has created yet another research area of interest, referred to as electrophilic and polycationic chalcogen chemistry [25]. Generally, the electron configuration of the chalcogens is represented as ns^2np^4 , with two electrons short of a filled valence shell [26, 27]. The properties of O, S, Se, Te, and Po are presented in **Table 1**.

On the one hand, while chalcophiles preferably form minerals with sulfur (**Figure 1**), selenium, and tellurium, on the other hand, their unique properties in forming new compounds and materials have created a paradigm shift in research interests focusing on the deep understanding of the chalcogens and their resultant compounds also known as chalcogenides.

A great variety of technological applications are now found for the many compounds of the elements of chalcogens [28–34]. This textbook emphasizes on this shift from not only fundamental chalcogen chemistry but also on the new shift to new chalcogen materials synthesis, characterization, and testing. These trends also include fundamental research works in other fields like those in coordination chemistry focusing on a large variety of ligands [20, 23]. This subfield explores ligands containing chalcogen atoms potentially suitable for the preparation of new precursors for metal-chalcogenide vapor deposition [7]. Two examples of these macromolecules with biological activity are metallo-enzymes containing multi-metallic centers as active sites for a number of catalytic reactions and chalcogen-containing mixed macrocycles with signaling functional groups as sensors for heavy metal-ion recognition [16].

The literature [35–37] provides a variety of chalcogen compounds and materials or chalcogenides, though not exhaustive. In naming a few, it is worthwhile mentioning the class of charge-transfer salts of chalcogen-rich molecules such as tetrathiafulvalene (TTF), 1,2-dichalcogenolenes, or the variegated area of metal chalcogenides, which are all of topical interest [38]. The details of many other interesting compounds are provided in the other chapters of this book. In the field of materials and their potential applications and as an illustration, published research results and discussion span from *n*-dimensional molecular conductors to magnets, to bistable switchable materials, and to non-linear optical (NLO) materials [39].

This textbook discusses chalcogen chemistry from a multidisciplinary approach which ranges from synthetic to structural and theoretical chemistry, organic to inorganic and

Property	Oxygen	Sulfur	Selenium	Tellurium	Polonium
Atomic mass (amu)	16.00	32.07	78.96	127.60	209
Atomic number	8	16	34	52	84
Atomic radius (pm)	48	88	103	123	135
Atomic symbol	O	S	Se	Te	Po
Density (g/cm ³) at 25°C	1.31 (g/L)	2.07	4.81	6.24	9.20
Electron affinity (kJ/mol)	−141	−200	−195	−190	−180
Electronegativity	3.4	2.6	2.6	2.1	2.0
First ionization energy (kJ/mol)	1314	1000	941	869	812
Ionic radius (pm) [†]	140 (−2)	184 (−2), 29 (+6)	198 (−2), 42 (+6)	221 (−2), 56 (+6)	230 (−2), 97 (+4)
Melting point/boiling point (°C)	−219/−183	115/445	221/685	450/988	254/962
Normal oxidation state(s)	−2	+6, +4, −2	+6, +4, −2	+6, +4, −2	+2 (+4)
Product of reaction with H ₂	H ₂ O	H ₂ S	H ₂ Se	None	None
Product of reaction with N ₂	NO, NO ₂	None	None	None	None
Product of reaction with O ₂	—	SO ₂	SeO ₂	TeO ₂	PoO ₂
Product of reaction with X ₂	O ₂ F ₂	SF ₆ , S ₂ Cl ₂ , S ₂ Br ₂	SeF ₆ , SeX ₄	TeF ₆ , TeX ₄	PoF ₄ , PoCl ₂ , PoBr ₂
Standard reduction potential (E ⁰ , V) (E ⁰ → H ₂ E in acidic solution)	+1.23	+0.14	−0.40	−0.79	−1.00
Type of oxide	—	Acidic	Acidic	Amphoteric	Basic
Valence electron configuration*	2s ² 2p ⁴	3s ² 3p ⁴	4s ² 4p ⁴	5s ² 5p ⁴	6s ² 6p ⁴

*Configuration shown in this table does not include filled d- and f-subshells.

[†]Cited values for the hexa-cations are for six-coordinate ions and these values are usually estimated.

Table 1. Selected properties of the Group 16 elements [26].

analytical chemistry [40], biological to material science and supramolecular chemistry. As such, it is suitable for scientists, technologists, students, as well as for those whose major interest is chalcogen chemistry, with particular interests in the chalcogen compounds and materials [41, 42]. This introductory chapter is followed by four chapters. The presentation of the chapters in this book is such that there is no arbitrary separation of theoretical concepts (reactivity), chemistry (organic and inorganic), and applications of chalcogens and chalcogen materials (or chalcogenides) while an effort has been made to stress all three grouping of ideas and facts equally. As such, in individual chapters, the authors have attempted to present the chemistry of the chalcogen(s) or chalcogenide(s) with enough discussion focusing on their structural bonding and reactivities in relation to their characterization and applications. In all the chapters, practical examples are provided insofar as possible in order to illustrate ideas.



Figure 1. A crystalline sulfur deposit. This sulfur deposit is located around a volcanic vent in Kilauea Crater, Hawaii, USA [14]; sulfur is very different from oxygen, and not very abundant; elemental sulfur is usually found in rock formations overlying salt domes, often accompanying petroleum deposits [26].

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