Acid-Base Properties of Sulfide–Sodium Systems

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Abstract

Investigations of sulfide – sodium systems of heavy non-ferrous metals and their associated minerals have played an important part in course of development of modern technologies of complex processing of compound raw materials and semiproducts. Crystallization of generated structures as complex compounds – thiosalts takes place during cooling of these alloys. The reaction $3(\text{NH}_4)_2\text{S} + \text{Sb}_2\text{S}_5 \rightarrow 2(\text{NH}_4)_3\text{SbS}_4$ is considered to be an example of acid-base interaction of substances which do not contain oxygen and hydrogen. Theory of acids and bases developed by M.I. Usanovich says that acidity (basicity) is a substance property, which is not connected with belonging to a certain class of compounds and is a functional characteristic of comparison of partners in a given reaction. Developing these ideas R.G. Pearson has introduced a notion of "hard" and "soft" acids and bases (HSAB) and formulated the basic principle postulating that "hard" acids preferably interact with "hard" bases, and "soft" acids – with "soft" bases. There are a number of suggestions in geological literature for the qualitative estimation of acid-base interaction in compounds which form basis of rocks. One of them, namely, acid-base characteristic that is conditional potential of ionization is the most applicable to thiosalts.

Introduction

Investigations of sulfide – sodium systems of heavy non-ferrous metals and their associated minerals have played an important part in course of development of modern technologies of complex processing of compound raw materials and semiproducts [1-3]. Inoculation of $\text{Na}_2\text{S}$ into alloys of metal sulfides causes an inhibition of semi-conducting properties and an increase in contribution of ionic conductivity as a result of its interaction with components of the system [4].

Crystallization of generated structures as complex compounds – thiosalts takes place during cooling of these alloys. The reaction $3(\text{NH}_4)_2\text{S} + \text{Sb}_2\text{S}_5 \rightarrow 2(\text{NH}_4)_3\text{SbS}_4$ is considered to be an example of acid-base interaction of substances which do not contain oxygen and hydrogen [5].

Here an acid function is belong to $\text{Sb}_2\text{S}_5$, that is expressed as attracting an anion by $\text{Sb}_2\text{S}_5 + 3\text{S}^- \rightarrow 2\text{SbS}^3_4$. A base function is left for $(\text{NH}_4)_2\text{S}$ which sends this anion to $(\text{S}^-)$. M.I.Usanovich has shown the complete analogy of sulfides interaction with acid-base interaction of metal oxides and oxygen anhydrides in process of generation of binary salts according to D.I. Mendeleev.

Theory of acids and bases developed by M.I. Usanovich says that acidity (basicity) is a substance property, which is not connected with belonging to a certain class of compounds and is a functional characteristic of comparison of partners in a given reaction. The theory, which has combined the theories of Bransted and Lewis into one and enlarged their limits, obtained recognition abroad and finds an application in our native science, in particular, in geochemistry, mineralogy, electrochemistry, chemistry of complex compounds [6-10]. Developing these ideas R.G. Pearson has introduced a notion of "hard" and "soft" acids and bases (HSAB) and formulated the basic principle postulating that "hard" acids preferably interact with "hard" bases, and "soft" acids – with "soft" bases [11]. This has allowed the nature of acid – base interaction, including both ionic ant donor – acceptor constituents, to be explained.

Generation and local concentration of the stable combinations of the most ionic or most covalent compounds, affinity of some elements to oxygen, and
other ones – to sulfur, native state of a number of elements in environment [7], and also presence of limited quantity of mineral groups (silicate-oxide, chalcogenide ones etc.) in nature, their selective distribution in earth's crust can be explained by this classification.

Further reaction between ammonium and stibium sulfides has become a classic example of acid-base interaction [5,6]. Obviously interaction in all sulfide-sodium systems (Na2S–MejSj) also has acid-base nature, where sodium sulfide plays the part of a base, and its partner (MejSj) – the part of an acid.

Quantitative characteristic of interaction is determined for every particular case by the nature of elements forming components of a binary system, i.e. by difference in their acid-base properties.

According to M.I. Usanovich [5] cations of elements are acids and therefore they must be rowed by their strength in a sequence in accordance with their position in D.I. Mendeleev Periodic System of Elements. For the first time M.I. Usanovich [5] has shown that an ionization potential of an element can be quantitative measure of a substance acidity. However, in that case it is difficult to take stock of constituents of covalent and other complex bonds.

K.B. Yatsimirski made an attempt [12] to use a difference between an ionization potential and a heat of hydration of cations as a covalent characteristic of cations and to describe interaction among "hard" acids and bases basically by coulomb characteristics, and interaction among "soft" ones – by molecular orbital characteristics. That division of an acidity into ionic and covalent one is very relative even within narrow limits of the discussed reactions because of large difference in values of coulomb characteristics (charge, atomic radius) and affinity to electron (potential of ionization). Later K.B. Yatsimirski has offered to use hydride affinity (Af) that is affinity to hydride-ion or fluoride affinity (Af), that is affinity to fluoride-ion to characterize a strength of acids and bases (Table 1). It goes from this sequence that acid-base interaction in compounds which form basis of rocks [13-15]. One of them, namely, acid-base characteristic that is conditional potential of ionization is the most applicable to thiosalts. V.A. Zharkov suggested it [8,14] and it is calculated in accordance with the equation:

\[ Y = \frac{\sum n_i J_i + \sum n_i E_j}{\sum n_i + \sum n_j} \]

where: Ji is an average potential of ionization of i–cation, kcal/gram-atom; Ej is an average value of affinity to an electron of j–anion, kcal/gram-atom; ni and nj – quantity of i–cations and j–anions in a compound.

According to V.A. Zharkov [14] a conditional potential of ionization (Y) is energy spent for ionization of neutral elements and molecules up to ions with oxidation level which they have in a compound. Quantitatively the potential "Y" expresses acid-base properties of minerals and compounds. The higher a value of "Y" is the more acidic properties with respect to its partner this substance has.

Results and discussions

Calculation of "Y" for sulfides (Table 1) has shown, that its values is monotonically increasing among sulfides in accordance with the position of metals forming them in D.I. Mendeleev's Periodic System of Elements. The conditional ionization potential "Y" characterizes "hardness" of acids–sulfides, which increases from Na2S to GeS2 (see: upper part of the Table1). It goes from this sequence that GeS2 is the most "hard" acid and Tl2S < Ag2S < Cu2S are less "hard" acids, i.e. relatively "soft" acids. The "soft" acids polarize easily and interacting with Na2S they produce salts which have an ionic bond. GeS2, 8 SnS2 and other "hard" sulfides produce compounds with covalent bond that is caused by configuration of electron shells of nS2 in Ge4+, Sn4+, Sb3+ and the others. This sequence of "hardness" of sulfides (Table 1) is coordinated with a row offered by Pearson for ions of elements in case of aqueous solutions [16-18].

Interaction of acids MejSnj with base Na2S results in the neutralization of their acidic properties. Thiosalts forming in this case become more "soft" acids in comparison with salt-former MejSnj. Values of the conditional potentials of ionization of thiosalts pMejSnjNa2S (lower part of the Table1) decrease with increasing coefficient q (q = 1→2, etc.) and in the
### Table 1

| Value of the conditional potentials of ionization and "hardness" of acids – sulfides as of ZhMKO ("hard" and "mild" acids and bases) of Pearson | Value of "γ" of formation, kJ/mol |
|---|---|
| | 41 | 144.2 | 157.1 | 168.3 |
| Cu2S | 3:1 | 137.3 | 138.9 | 144.4 |
| FeS | S | S | S | S |
| | 1:1 | 19.9 | 19.9 | 19.9 |
| | 1:2 | 117.4 | 11.7 | 11.7 |
| | 1:3 | 121.7 | 121.7 | 121.7 |
| | 1:n | 148.9 | 148.9 | 148.9 |
| | S = soft, I = intermediate, H = hard (base) | | | |

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limit they approach to the value of "Y" for Na2S (112 kcal/mol), that determine cessation of acid-base interaction of a thiosalt with salt-former (for example Tl2S (127.2) > Tl2S-Na2S (119.9) > Tl2S-2Na2S (117.4) > Na2S (112.5 kcal/mol)). Cations of transition metals having d-electron shells polarize easily, for example Cu+: Cu2S (152.1 kcal/mol) > 4Cu2S-Na2S (144.2) > 2Cu2S-Na2S (138.9) > Cu2S-9Na2S (116.3) > Na2S (112.5 kcal/mol). Analogous picture is for Ag2S.

Thiosalts of "hard" and sulfides closed to them (SnS2, Sb2S3, As2S3, PbS, Bi2S3) having the maximal coefficient "q" are closed to salt-farmers Cu2S (152.1) and Ag2S (149.8) according to their acid properties. Probably these thiosalts can be referred to relatively "soft" acids. Taking into consideration the configuration of nS2 electron shells it can be possible to foresee an existence of mixed (ionic – covalent) character of the bond.

Conclusions

Apparently this is connected with the structure of complex anion [pMenSm.qS2-]i, which is polymerized due to bridge bond of sulfur. Because of physical reasons, mobility of such ions must be small enough. So use of the values of the conditional ionization potential "Y" and Pearson principle of HSAB allows this question to be partially answered when there is no practical possibility to determine stability and structure of sodium thiosalts with the help of thermodynamics.

In the sequence of sulfides according to increasing values of their ionization potentials "Y", sulfides being at the beginning of this sequence and having small values of "Y", from Tl2S to Cu2S can be referred to "soft" acids with an ionic bond. Further, sulfides from PbS to Sb2S, Bi2S3 can be referred to the intermediate type of acidity, and Jn2S3, As2S3, SnS2, GIS2 – to "hard" acids predominantly in various degrees with covalent type of bond.

Alloys of sodium thiosalts having low values of "Y" and belonged to "soft" or intermediate acids, have mainly ionic type of bond that allows electrolysis with production of a metal directly on an electrode to be carried out [4, 19-22].

References

1. Polyvyannyi I.R., Demchenko R.S., Electrotermics in metallurgy of lead. Alma-Ata. 1971. p. 315.
2. Polyvyannyi I.R., Demchenko R.S. Chemistry and technology of thiosalts of non-ferrous metals. Proceedings of IMIO of AN KazSSR, Alma-Ata, 1967.
3. Complex processing of mineral raw materials by the methods of alkali metallurgy. Abstracts of the reports of the Third Republican Conference. Alma-Ata. 1987. p. 307.
4. Velikanov A.A., Eichis B.A., Bulletin of the Higher Institutes of Learning. Non-ferrous metallurgy, 1971, No. 2, pp. 42-44.
5. Usanovich M.I. Bulletin of the general chemistry, 1939, 9, p.182.
6. Clide Day M., Serbin D. Theoretical inorganic chemistry. M: Khimiya, 1969, p. 335.
7. Urusov V.S. Energetic crystallochemistry. M, Nauka, 1975, pp. 225-255.
8. Acid-base properties of chemical elements, minerals, rocks and natural solutions. Editors: Marakushev A.A. and Rakcheev A.D., M, Nauka, 1982, p. 216.
9. Yatsimirski K.B. Acid-base and donor-acceptor properties of ions and molecules. Theoretical and experimental chemistry, 1970, 6, No. 4, p. 462.
10. Yatsimirski K.B. Characteristics of hardness and softness of acids obn the base of their affinity to anions and to electron. Journal of general chemistry, 1983, T. 53, (115) Issue 8, p. 1885.
11. Pearson R.G. Hard and soft acids and bases, HSAB. J.Chem.Educ. 1968, V. 45, pp. 581-587.
12. Yatsimirski K.B. Concerning problem of change of free energy and enthropy during reactions of complex formation. Journal of Physiscal Chemistry, 1951, T. 25(2), p. 221.
13. Korzhinski D.S. Regime of acidity of hydrothermal solutios. Izvestiya AN USSR. Serie geol., 1957, No. 12, p. 35.
14. Zharikov V.A., Acid-base characteristics of minerals. Geology of ore deposits, 1967, No. 5, p. 75.
15. Godovikov A.A. Percularities of composition, systematics and certain features of genesis of natural oxides ad silicates. Izv. AN USSR. Ser. Geol., 1977, No. 1, p. 14.
16. Pearson R.G. J. Amer. Chem Soc. 1963, V. 84, p.3533.
17. Pearson R.G. Rep. From chemistry in Britain, 1967, v. 3, p.103.
18. Pearson R.G. J. Amer. Chem. Soc. 1968, v. 77, p. 238
19. Mustyatsa O.N. Velikanov A.A. Electrochemistry, 1971, T. 7, No. 12, p. 1805
20. Eichis B.A., Sokolov T.G., Velikanov A.A. Electrochemistry, 1971. T. 7, No. 10, p. 1499.
21. Belous A.N., Omelchuk A.A., Mironyuk G.I., Works of the First Ukraininan republican conference in electrochemistry. 4.II, Kiev, Naukova dumka, 1973, p. 25
22. Velikanov A.A., Mustyatsa O.N., Mironyuk G.I., Electrochemical technology, 1974, No. 5, p. 59
23. Kopylov N.I., Lata V.A., Toguzov M.Z., Interactions and phase states in sulphide systems melts. Ust-Kamernogorsk, "Gylym" 2001, p. 436.

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