

## 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  $3(NH_4)_2S + Sb_2S_5 \rightarrow 2(NH_4)_3SbS_4$  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  $Na_2S$  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  $3(NH_4)_2S + Sb_2S_5 \rightarrow 2(NH_4)_3SbS_4$  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  $Sb_2S_5$ , that is expressed as attracting an anion by  $Sb_2S_5$  ( $Sb_2S_5 + 3S^{2-} \rightarrow 2SbS^{3-}_4$ ). A base function is left for  $(NH_4)_2S$  which sends this anion to  $(S^{2-})$ . M.I.Usanovich has shown the complete analogy of sulfides interaction

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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 and 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 ( $Na_2S-Me_nS_m$ ) also has acid-base nature, where sodium sulfide plays the part of a base, and its partner ( $Me_nS_m$ ) – 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 ( $A_H$ ) that is affinity to hydride-ion or fluoride affinity ( $A_f$ ), that is affinity to fluoride-ion to characterize a strength of acids and bases and their "hardness – softness" under donor – acceptor interaction [12].  $A_H$  characterizes "softness" and  $A_f$  – "hardness" of bases. Difference  $\Delta A_{fH} = A_f - A_H$  shows the tendency of a cation to form both ionic or covalent bonds: there is ionic bond if  $\Delta A_{fH} > 0$ , and there is covalent (donor – acceptor) one if  $\Delta A_{fH} < 0$ .

All these suggestions to estimate the strength of acid – base interaction are correct for aqueous or gaseous media. There are a number of suggestions in geological literature for the qualitative estimation

of 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. Zhariikov suggested it [8,14] and it is calculated in accordance with the equation:

$$Y = \frac{\sum n_i J_i + \sum n_j E_j}{\sum n_i + \sum n_j},$$

where:  $J_i$  is an average potential of ionization of  $i$  – cation, kcal/gram-atom;  $E_j$  is an average value of affinity to an electron of  $j$  – anion, kcal/gram-atom;  $n_i$  and  $n_j$  – quantity of  $i$  – cations and  $j$  – anions in a compound.

According to V.A. Zhariikov [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  $Na_2S$  to  $GeS_2$  (see: upper part of the Table1). It goes from this sequence that  $GeS_2$  is the most "hard" acid and  $Tl_2S < Ag_2S < Cu_2S$  are less "hard" acids, *i.e.* relatively "soft" acids. The "soft" acids polarize easily and interacting with  $Na_2S$  they produce salts which have an ionic bond.  $GeS_2$ ,  $8 SnS_2$  and other "hard" sulfides produce compounds with covalent bond that is caused by configuration of electron shells of  $nS_2$  in  $Ge^{4+}$ ,  $Sn^{4+}$ ,  $Sb^{3+}$  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  $Me_nS_m$  with base  $Na_2S$  results in the neutralization of their acidic properties. Thiosalts forming in this case become more "soft" acids in comparison with salt-former  $Me_nS_m$ . Values of the conditional potentials of ionization of thiosalts  $pMe_nS_qNa_2S$  (lower part of the Table1) decrease with increasing coefficient  $q$  ( $q = 1 \rightarrow 2$ , *etc.*) and in the

**Table 1**  
Values of the conditional potentials of ionization and "hardness" of acids – sulfides as of ZhMKO ("hard" and "mild" acids and bases) of Pearson

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Sulfide of an element	Na <sub>2</sub> S	< Ti <sub>2</sub> S	< Ag <sub>2</sub> S	< Cu <sub>2</sub> S	< PbS	< FeS	< CoS	< CdS	< ZnS	< In <sub>2</sub> S <sub>3</sub>	< Sb <sub>2</sub> S <sub>3</sub>	< Bi <sub>2</sub> S <sub>3</sub>	< As <sub>2</sub> S <sub>3</sub>	< SnS <sub>2</sub>	< GeS <sub>2</sub>
Hardness/mildness of cations of elements according to Pearson [16-18]	S	S	S	S	I	I	I	S	I	H	I	I	H	H	H
Value of "Y" of sulfide of an element, kcal/mol	112.5	127.2	149.1	152.1	179.4	188.8	193.7	198.7	207.7	214.0	214.9	217.3	234.5	245.6	264.3
Ratio in thiosalt (p/q)	Value of "Y" of thiosalt, kcal/mol														
4:1				144.2											
3:1					157.1										
2:1			137.3	138.9		146.3*									213.0
3:2			134.8											225.7	
1:1		119.9				(43) 148.5		147.1	150.5	180.5	176.4	184.2	188.7	179.0	205.2
2:3							(57) 138.6				166.3			165.7	173.3
1:2		117.4					(49) 130.9	134.1						156.8	
1:2.5						128.0									
1:3			121.7					128.2	129.7		148.9	146.0	156.0		
1:n				(19) 116.3						(14) 144.4					
(at n > 3)										(15) 139.6					

S – soft, I – intermediate, H – hard (base)  
\* – Cu<sub>2</sub>S/FeS/Na<sub>2</sub>S

limit they approach to the value of "Y" for  $Na_2S$  (112 kcal/mol), that determine cessation of acid-base interaction of a thiosalt with salt-former (for example  $Tl_2S$  (127.2) >  $Tl_2S \cdot Na_2S$  (119.9) >  $Tl_2S \cdot 2Na_2S$  (117.4) >  $Na_2S$  (112.5 kcal/mol)). Cations of transition metals having *d*-electron shells polarize easily, for example  $Cu^+$ :  $Cu_2S$  (152.1 kcal/mol) >  $4Cu_2S \cdot Na_2S$  (144.2) >  $2Cu_2S \cdot Na_2S$  (138.9) >  $Cu_2S \cdot 9Na_2S$  (116.3) >  $Na_2S$  (112.5 kcal/mol). Analogous picture is for  $Ag_2S$ .

Thiosalts of "hard" and sulfides closed to them ( $SnS_2$ ,  $Sb_2S_3$ ,  $As_2S_3$ ,  $PbS$ ,  $Bi_2S_3$ ) having the maximal coefficient "q" are closed to salt-formers  $Cu_2S$  (152.1) and  $Ag_2S$  (149.8) according to their acid properties. Probably these thiosalts can be referred to relatively "soft" acids. Taking into consideration the configuration of *nS*<sub>2</sub> 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  $[pMe_nS_mqS^2]^-i$ , 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  $Tl_2S$  to  $Cu_2S$  can be referred to "soft" acids with an ionic bond. Further, sulfides from  $PbS$  to  $Sb_2S_3$ ,  $Bi_2S_3$  can be referred to the intermediate type of acidity, and  $Jn_2S_3$ ,  $As_2S_3$ ,  $SnS_2$ ,  $Gls_2$  – 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].

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