Department of Materials Science and Engineering

Phase Equilibria and Thermochemistry of Selected Sulfide Systems in the Pyrometallurgy of Ni and Cu

Fiseha Tesfaye, Pekka Taskinen

Aalto University

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Abstract

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Abstract

A review of phase equilibria and thermodynamic data of Ni-(As, Se)-S and Cu-(As, Bi, Pb, Sb, Se, Te, Nb, Zn, Mo)-S systems was done. Particular emphases were given to the compilation and refine of the standard Gibbs energies of formations of equiliblium phases, which are of interest in the pyrometallurgical processes of copper and nickel production. Phase stabilities, phase relations and solubility limits of some equilibrium phases in the Ni-(As, Se)-S and Cu-Mo-Bi-Nb-S systems were also compiled and reviewed, based on the available literature.

This work also reviews, updates, and extends the earlier reports. The Gibbs energies of formations and reactions are mostly presented as linear equations, in each temperature ranges of phase stabilities. List of thermal stabilities of some pure sulfides and sulfosalts were also reviewed and compiled (Appendix).

Keywords Cu, Ni, sulfide, sulfosalt, thermodynamics, phase equilibrium

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Symbols, Abbreviations, Units

G, (g), V	gas phase, vapor
L, (l)	liquid
s	solid
(s, l)	solid or liquid based on the temperature condition
T	temperature [K]
T_m	melting temperature [K]
T_{max}	maximum temperature of stability [K]
T_{liq}	liquidus temperature [K]
T_{sol}	solidus temperature [K]
x_i	composition of component i
ss	solid solution
ΔG_f^o	standard Gibbs energy of formation [J/mol]
ΔG_r	standard Gibbs energy of reaction [J/mol]
ΔG_{mix}	Gibbs energy of mixing [J/mol]
ΔH_{mix}^o	heat of mixing [J/mol]
ΔS_{mix}^o	entropy of mixing [J/mol.K]
R	8.314472(15) [J/mol.K]
T(K) – T(^{o}C)	273.15
J/cal.	4.1868

1 Introduction

Due to increasing association of impurities in the copper and nickel ore minerals and concentrates, the production of high grade Cu and Ni by the conventional pyrometallurgical processes is compromised. Thus, smelters are in need to modify their operating flow sheets and strategies for processing more complex feed materials economically, while meeting the strict environmental regulations. To make the appropriate modifications, a thorough evaluation of the thermochemistry and thermal stabilities of phases and phase assemblages existing in these complex ore minerals is essential.

In the previous reports [3, 4, 5, 6], the phase equililibria and thermodynamic properties of the pure binary sulfides in the (Fe, Ni, Cu, Zn)-S systems and their ternaries as well as the (Ni, Cu)-(As, Sb)-S, Cu-Bi-S and Zn-As-Cu-Pb-S systems were discussed. In this report, phase relations in the Ni-As-Se-S system, for which the phase equilibria studies were not included in the previous reports were reviewed. Experimental data and estimates of standard Gibbs energies of formations and reactions of equiliblium phases in the systems which are studied in this and earlier reports are refined and summarized in chapter 3. Thermal stabilities of some pure sulfides and sulfosalts (including the previous studies) are also compiled (see Appendix).

The main purpose of this study was to selectively review and compile thermodynamic properties of equilibrium phases and their assemblages that are of interest in the pyrometallurgical processes of copper and nickel production. The intention was to contribute to the evaluation of the behavior of impurities in copper and nickel minerals and concentrates processing operations.

1.1 Gibbs Energies of Formations of the Sulfosalts

Most sulfosalts may be regarded as intermediate phases on the joins between simple sulfide components. For instance, sulfosalts in the Pb-Bi-S and Ag-Bi-S systems lie on the joins PbS-Bi_2S_3 and Ag_2S-Bi_2S_3, respectively.

Therefore, the chemical compositions of the sulfosalts are, in general, stoichiometric, having formula consistent with normal valences of the elements. Furthermore, many of the structures are similar to those of the component simple sulfides such as galena-like and stibnite-like layers in lead sulfantimonides [7].

The sulfosalts constitute a large and complex group of ore minerals. Although the sulfosalts rarely form massive ore bodies, they have proven sources of valuable metals. They are commonly encountered with rich sulfide ores of Ag, Cu, Pb, Fe and Ni; and they are widely distributed in poor mineral rocks [8]. However, thermochemical data for the sulfosalt minerals are available only for few systems and experimentally determined thermodynamic properties are limited.

By combining new and old data from the literature regarding the thermodynamic functions of the sulfosalt minerals, with a few simple assumptions, may permit calculation of new thermochemical data for a number of sulfosalt minerals that are well characterized. As these data are working approximations, they must be refined for tasks that require greater accuracy.

2 Phase Equilibria

Phase relations in (Ni, Cu, Zn)-S, (Ni, Cu)-(As, Sb)-S, Cu-Bi-S and Zn-As-Cu-Pb-S sulfide systems were discussed in the previous reports [3, 4, 5, 6]. In this study, phase equilibria in the Ni-As-Se-S and Cu-Mo-Nb-Bi-S systems, which were not included in the previous reports, will be selectively discussed. Thermal stabilities of some pure sulfides and sulfosalts (including the previous studies) are also compiled (Appendix). Gibbs energies of formation of the equilibrium phases for which experimental data or estimates are available in the broader system (including phase equilibria studied in the previous works) were reviewed and compiled in chapter 3 (Table 4).

2.1 The Ni-As-Se-S System

Minerals and compounds in the Ni-As-S system are maucherite ($Ni_{11}As_8$), niccolite ($Ni_{1\pm x}As$), $NiAs_2$-polymorphs (rammelsbergite and pararammelsbergite), Ni_5As_2, vaesite (NiS_2), polydymite (Ni_3S_4), millerite ($Ni_{1-x}S$), heazlewoodite (Ni_3S_4), $Ni_{3\pm}xS_2$, Ni_7S_6, orpiment (As_2S_3), realgar (AsS) and Gersdorffite with a wide compositional range (NiAsS). Details about their phase relations were reviewed in [4, 5] and their thermodynamic properties are summarized in chapter 3 and Appendix. In this section, phase equilibria of the systems As-Se-S and Ni-Se will be discussed.

2.1.1 Ni-Se

This system is comprised of five intermediate binary phases, as listed in Table 1. The melting temperature of Ni (1455.15 ^{o}C) and Se (220.85 ^{o}C) was taken from [9]. An assessed phase diagram of the Ni-Se system by Lee & Nash [10] is shown in Figure 1. In a study based on measurements of lattice parameter, Kuznecov [11] reported the solubility of Se in (Ni) at 620 ^{o}C to be less than 0.1 at. % Se. A metastable phase α'Ni_2Se_3 has also been reported by Kuznecov [11] as a polymorphic transitions α'$Ni_2Se_3 \leftrightarrow \beta Ni_2Se_3$ and $\alpha Ni_2Se_3 \leftrightarrow \alpha$'$Ni_2Se_3$ at 620 ^{o}C and 590 ^{o}C, respectively.

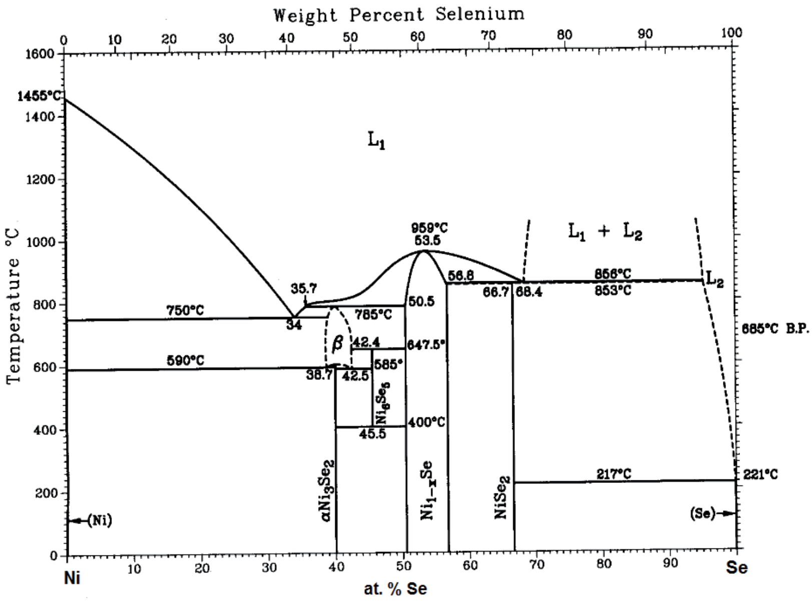

Figure 1. The Ni-Se phase diagram [12].

Table 1. Phase transformation reactions in the Ni-Se system [10, 9]. Composition of Se is written according to the arrangement of phases in the reactions.

Reaction	at. % Se	T(°C)	Reaction type	Ref.
Ni ↔ L	0	1455.2	Melting	[9]
$\beta Ni_{3\pm x}Se_2$ ↔ α Ni_3Se_2	40	600	Polymorphic	[10]
$Ni_{1-x}Se$ ↔ L	53.5	959	Congruent	[10]
(Ni) + β ↔ L1	0 39.2 34	750	Eutectic	[10]
(Se) + $NiSe_2$ ↔ L2	100 | 66.7 | 100	217	Eutectic	[10]
Ni_6Se_5 ↔ α Ni_3Se_2 + α $Ni_{1-x}Se$	45.5 | 40 | 50.5	400	Eutectoid	[10]
$\beta Ni_{3\pm x}Se_2$ ↔ (Ni) + α Ni_3Se_2	38.7 | 0 | 40	590	Eutectoid	[10]
$\beta Ni_{3\pm x}Se_2$ ↔ α Ni_3Se_2 + Ni_6Se_5	42.5 | 40 | 45.5	585	Eutectoid	[10]
L1 + $Ni_{1-x}Se$ ↔ βNi_3Se_2	35.7 | 50.5 | 40	785	Peritectic	[10]
$Ni_{1-x}Se$ + L2 ↔$NiSe_2$	56.8 | 95.1 | 66.7	~ 853	Peritectic	[10]
$\beta Ni_{3\pm x}Se_2$ + $Ni_{1-x}Se$ ↔ α Ni_6Se_5	42.4 | 50.5 | 45.5	647.5	Peritectoid	[10]
L1 ↔ $Ni_{1-x}Se$ + L2	68.4 | 56.8 | 95.1	856	Monotectic	[10]
Se ↔ L	100	220.85	Melting	[9]

2.1.2 As-S-Se

Partial phase diagram of the As-Se system, in the composition range 40 – 100 wt. % Se, is shown in Figure 2. An optimized condensed phase diagram of the Se-As system along with selected experimental points is shown in Figure 3. Amorphous Se undergoes a glassy transition at about 30.25 °C [13]. Mass-spectrometric studies by Drowart et al. [14] revealed the presence of Se_1 to Se_8 species in the vapor. According to their results Se_2, Se_5, Se_6, and Se_7 are the major species depending on the temperature.

Dembovskii and Luzhnaya [15] studied the Se-As system by DTA for compositions up to about 70 mol. % As. Consequently, they found two congruently melting compounds, As_2Se_3 and AsSe. According to Blachnik et al. [16], AsSe melts peritectically at 264 °C, rather than congruently at 295 °C [15], and the polymorphic transition temperature of As_4Se_3 is 174 °C. Myers and Felty [17] employed static quench techniques to study the phase diagram for compositions up to 60 mol. % As. No details of the experiments and no experimental points were given, however, from their phase diagram the invariant points are derived and collected in Table 3. A result of X-ray analysis indicated that AsSe crystallizes in the realgar structure, which corresponds to the formula As_4Se_4 [13].

By using the Fluorine-combustion calorimetry method, O'Hare et al. [18] determined the enthalpy of the transition from vitreous to the crystalline forms of As_2Se_3 to be −(28.0 ± 3.9) kJ/mol., at 298.15 K, and $\Delta_f H_m^o$ (As_2Se_3, crystalline) = −(86.1 ± 4.1) kJ/mol. and $\Delta_f H_m^o$ (As_2Se_3, vitreous) = −(58.1± 4.2) kJ/mol., both at standard conditions. According to O'Hare et al. [18] the melting temperature of As_2Se_3 is about 359.85 °C. Enthalpies of high-temperature decomposition of As_2Se_3 along with derived molar heats of formation, at room temperature are shown in Table 2.

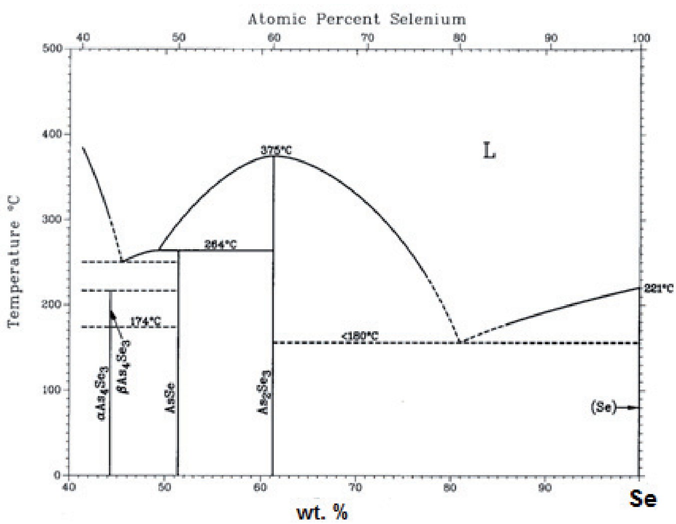

Figure 2. The As-Se phase diagram [12].

Table 2. Enthalpies of high-temperature decomposition of As_2Se_3 and derived $\Delta_f H_m^o$ values at 298.15 K [18, 19]. For the derivation of $\Delta_f H_m^o$ (As_2 Se_3 (s), kJ/mol), the following auxiliary values were used: $\Delta_f H_m^o \left(As_4(g), \frac{kJ}{mol} \right) = 158.2 \pm 2.5$ and $\Delta_f H_m^o \left(Se_2(g), \frac{kJ}{mol} \right) = 144.1 \pm 0.6$.

Reaction	$\Delta_r H_m^o$ (kJ/mol) [19]	$\Delta_f H_m^o$ (As_2 Se_3 (s), kJ/mol) [18]
As_2Se_3(vit) = ½As_4Se_3(g) + $\frac{3}{4}Se_2(g)$	222.8 ± 8.0	-59 ± 9
½As_4(g) + $\frac{3}{4}Se_2(g)$ = ½As_4Se_3(g)	-131.3 ± 3.0	-
As_2Se_3(vit) = ½As_4Se_4(g) + $\frac{1}{2}Se_2(g)$	177.8 ± 7.0	-49 ± 8
½As_4(g) + $Se_2(g)$ = ½As_4Se_4(g)	-166.5 ± 3.0	-
As_2Se_3(s) = ½As_4Se_3(g) + $\frac{3}{4}Se_2(g)$	259.4 ± 8.0	-95 ± 9
As_2Se_3(s) = ½As_4Se_4(g) + $\frac{1}{2}Se_2(g)$	219.7 ± 7.0	-91 ± 8

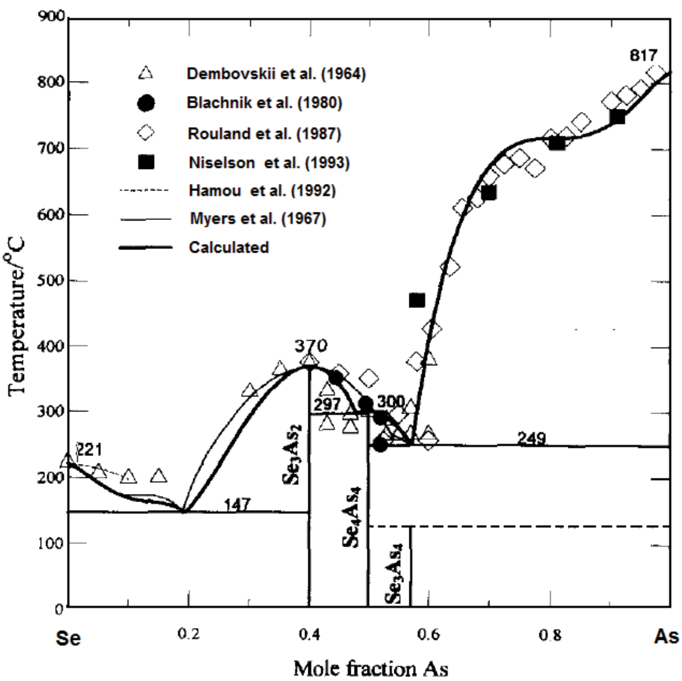

Figure 3. A condensed phase diagram of the System As-Se [13].

Phase diagram of the S-Se system is shown in Figure 4. Solid sulfur exists in two allotropic forms α-S, stable up to 95.5 °C, and β-S, stable from 95.5 °C to its melting point (115.22 °C) [20]. Se exists in one crystal structure form up to its melting point at 221 °C [9, 20]. The phase diagram is essentially determined by Ringer [21] by thermal and dilatometric methods. Sharma and Chang [20, 22] have made modifications with regard to the then accepted melting points of S and Se. In addition to the primary solid solutions (αS), (βS) and Se, there exists an intermediate phase, γ, with a wide composition range (48.7 – 83 at. % Se) [22]. The invariant points in this system are also collected in Table 3.

According to Boudreau and Haendler [23] there exists several metastable phases in the S-Se system, mostly based on the known structures of S and Se. Geller and Lind [24] reported a triagonal phase $S_{0.555}Se_{0.455}$ to form when equiatomic compositions are mixed and subjected to a pressure of 20 Kbar at 280 °C.

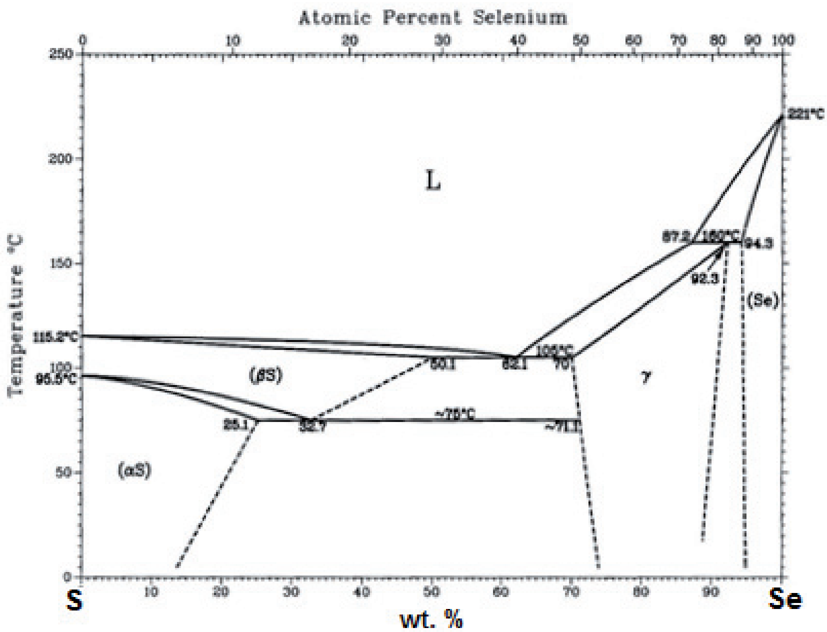

Figure 4. The S – Se phase diagram [20].

Phase relations in the As_2S_3 – As_2Se_3 system have been studied by the DTA method, using a Kurnakov pyrometer with Pt-PtRh thermocouples, by Zhukov et al. [25]. They studied end-members of six intermediate compositions (10, 25, 35, 55, 75, 95 mol% As_2Se_3). Their results showed that the system forms a continuous series of solid solutions (ss), as shown in Figure 5, and the glass transition temperature for the whole system is constant and occurs at 180 ± 5 °C.

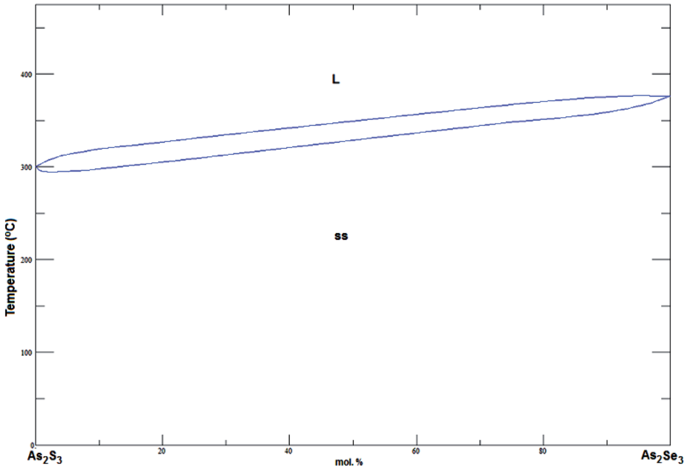

Figure 5. Phase relations in the As_2S_3 – As_2Se_3 system [26].

Table 3. Phase change reactions in the As-Se and S-Se systems [9, 22, 27]. Composition of Se is written according to the arrangement of phases in the reactions. The composition range for γ is 48.7 – 83 at. % Se.

Reaction	at. % Se	T(°C)	Reaction type	Ref.
L ↔ βS	0	115.22	Melting	[22]
βS ↔ αS	0	95.5	Allotropic	[22]
(βS) ↔ (αS) + γ	16.5 |12 | ~50	75	Eutectoid	[22]
L ↔ (βS) + γ	40 |29 | 48.7	105	Eutectic	[22]
L + (Se) ↔ γ	73.5 |87 | 83	160	Peritectic	[22]
Se ↔ L	100	220.85	Melting	[9]
L ↔ Se + As_2Se_3	-	146	Eutectic	[27]
As_2Se_3 ↔ L	60 | -	370	Congruent melting	[27]
L + As_2S_3 ↔ As_4Se_4	-	265	Peritectic	[27]
L ↔ As_4Se_4 + As	-	250	Eutectic	[27]

2.2 The Cu-Mo-Bi-Nb-S System

Phase relations in the Cu-Bi-S system have been reviewed in the previous report [5]. There are no intermediate phases in the metal-metal systems; Cu-Mo [28], Cu-Bi [12], Mo-Nb [12], Mo-Bi [12], Nb-Bi [12] and Cu-Nb

[30], and in this section phase relations in the Cu-Mo-Bi-S and Cu-Nb-S systems will be discussed. The Gibbs energies of formations and sulfidation reactions of some the stable phases are summarized in chapter 3.

2.2.1 Cu-Mo-Bi-S System

A review of phase relations in this system is done through two major systems Mo-Bi-S and Cu-Mo-S.

2.2.1.1 Mo-Bi-S

Mo melts at high temperature of 2622.85 °C [9]; consequently, the lowest melting point of its sulfides is above 1450 °C. Phase diagram of the Mo-S system obtained by thermodynamic modeling is shown in Figure 6. According to Brewer & Lamoreaux [29], the system is characterized by two stable intermediate phases Mo_2S_3 (mP10) and MoS_2 (hP6). Sulfur rich amorphous phase, MoS_3, was reported to have been prepared by decomposition of sulfomolybdates. The amorphous phase transforms to $Mo_{0.83}S_2$ up on heating above 200 °C [30].

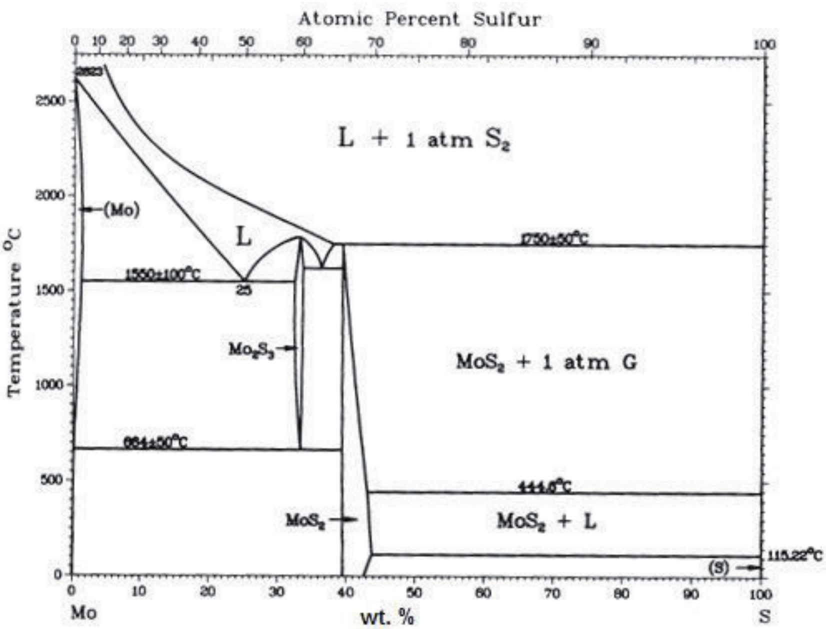

Figure 6. The Mo-S phase diagram [12].

While studying the Sn, W and Mo type of ores, Stemprok [31] reported native Bi, Bi_2S_3 and MoS_2 to occur in association with ore minerals such as cassiterite (SnO_2), wolframite (WO4), arsenopyrite (FeAsS), chalcopyrite

($CuFeS_{2-x}$) and pyrite (FeS_2), where quartz, micas, topaz, tourmaline, and fluorite are the main gangue minerals.

Phase relations in the Mo-Bi-S system, below the crystallization temperature of Bi_2S_3, 760 °C [31], are shown in Figure 7 and Figure 8. There exists a tie line between Bi_2S_3 and MoS_2. The Bi-S liquid field decreases in extent with decreasing temperature. At about 610 °C the Mo_2S_3 phase becomes unstable, and below this temperature MoS_2 coexists with metallic Mo. The phase relations slightly below the 610 °C are shown in Figure 7. Below the melting point of Bi (271.4 °C [9]) close to the corner of pure Bi, eutectic exists at about 270 °C [12]. According to Stemprok [31], experiments in which small amounts of MoS_2 were added to Bi-S mixtures of a composition near the binary eutectic did not result in any melt formation below 267 °C, which indicates that a ternary eutectic does not exist.

The solubility of MoS_2 and Mo_2S_3 in liquid Bi investigated by Stemprok [31], at temperatures between 400 - 1200 °C, have been shown to be considerably less than 1 wt. %. Similarly, the solubility of MoS_2 in Bi_2S_3 (s), at 700 °C, and in Bi_2S_3 (l), at 920 °C, are less than 1 wt. %. Likewise, the solubility of Bi and Bi_2S_3 in MoS_2 at 700 °C are less than 1 wt. %. The maximum Bi content of MoS_2 is 0.24 wt. % [31] and the Mo content of native Bi and Bi_2S_3 was reported to be about 0.00002 wt. % [32].

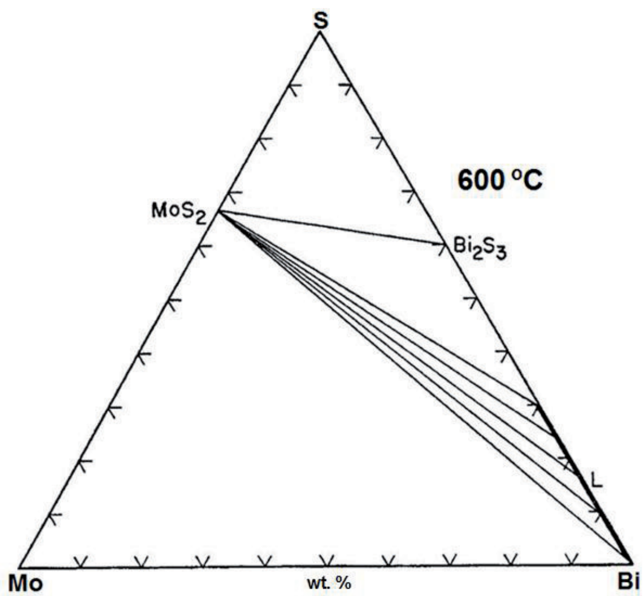

Figure 7. Phase relations in the Mo-Bi-S system at 600 °C. The solubility of molybdenite (MoS_2) in liquid L is much less than 1 wt. % [31].

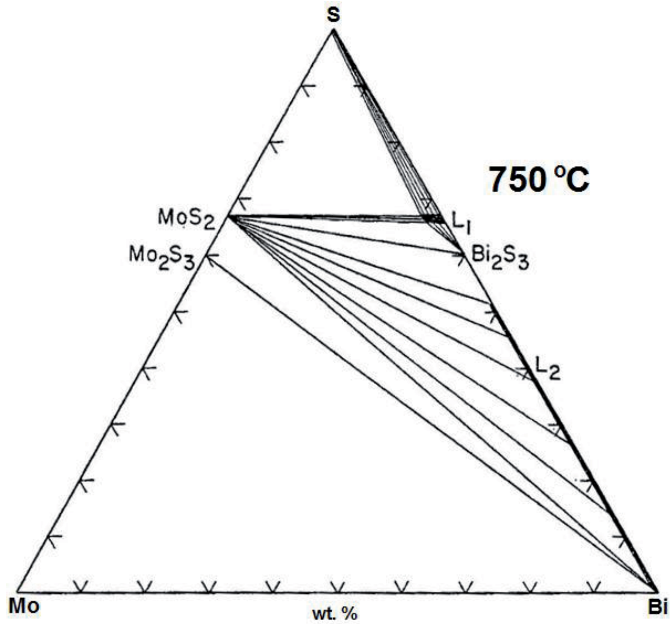

Figure 8. Phase relations in the Mo-Bi-S system at 750 °C. The solubility of molybdenite (MoS_2) in liquid L_1 was slightly exaggerated to reveal the phase relations. Tie line between MoS_2 and Bi_2S_3 prohibits equilibrium coexistence of Mo_2S_3 and Bi_2S_3 [31].

2.2.1.2 Cu-Mo-S

Phase relations in the binary Mo-S system were discussed in section 2.2.1.1. The ternary phase relations in the Cu-Mo-S system have been investigated by Grover [33] and Grover & Moh [34]. According to their studies, at about 1000 °C a miscibility gap between the sulfur-rich and sulfide-rich melts exists close to the Cu-S binary.

According to Chang et al. [30], the Cu-Mo-S system comprises a single ternary phase; ~$CuMo_2S_3$, with small homogeneity range and thermal stability range between 594 and > 1000 °C, which was characterized by Grover [33]. Below 813 °C, a sulfide-rich liquid of ~1 wt. % Mo cease to exist and $Cu_{2-x}S$ phase coexists with S-rich liquid (L1) as shown in Figure 9. As temperature decreases, the homogeneity range of ~$CuMo_2S_3$ narrows and at 685 °C the following equilibrium can be expressed as Reaction (I):

$Cu_{2-x}S$ + ~$CuMo_2S_3$ (17.8 wt. % Cu, 27.4 wt. % S, 54.8 wt. % Mo) = (Cu) + MoS_2. (I)

Below about 594 °C, the ternary phase does not any more exist [30].

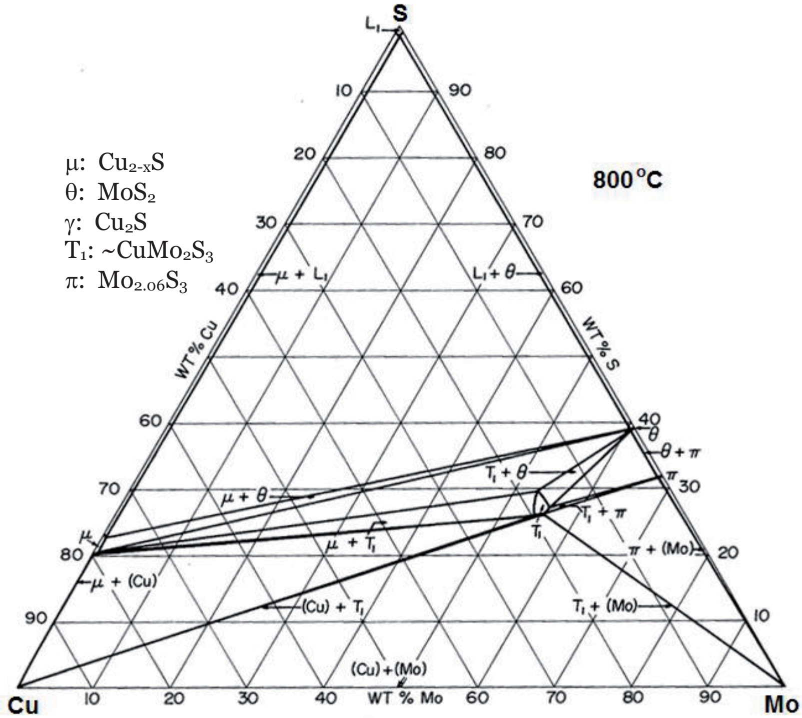

Figure 9. Phase relations in the Cu-Mo-S system at 800 °C [30].

2.2.2 Cu-Nb-S System

A large number of Nb-sulfides are reported in the literature. Biltz and Kocherz [35] noted the presence of $NbS_{0.5-1.0}$, Nb_2S_3, and NbS_2. Jellinek [36, 37] disputes these early results and instead reporte the 'stable' phases NbS_3, NbS_2 (rhomb.), NbS_2 (hex.), $Nb_{1+x}S_2$ (rhomb.), and $Nb_{1+x}S_2$ (hex.). Hodouin [38] notes the formation of NbS, Nb_3S_4, $Nb_{1+x}S_2$ (hex.), $Nb_{1+x}S_2$ (rhomb.), and NbS_2 at 1273 K. Hartman and Wagner [39] reported the formation of Nb_4S_7. Presently, there are discrepancies in the phase limits reported by various authors in addition to the particular compounds present at equilibrium.

The Nb-S phase diagram redrawn by Massalski [12] from [40] is shown in Figure 10. According to [9] Nb melts at 2476.85 °C. Selected stable intermediate phases reported by different researchers in the system are $Nb_{14}S_{15}$ [41], $Nb_{21}S_8$ [40], $Nb_{10}S_9$ [40], NbS [42], Nb_3S_4 [35, 40], NbS_2 [35, 40] and NbS_3 [40]. NbS exists in two modifications (hexagonal) α-NbS and (orthorhombic) β-NbS. The α- to β-NbS transition is reported to take place at 780 °C on heating and at 740 °C on cooling [42]. NbS_2 also occurs in two forms (rhombohedral) α-NbS_2 (stable below 850 °C [40]) and (hexagonal) β-NbS_2 (stable in the temperature range ~850 – 1050 °C [37]). Except Chen's et al. [41] report for $Nb_{14}S_5$ to melt at slightly above 1500 °C, the melting points of the intermediate phases are not available.

No intermediate phases appear in the Cu-Nb system [30]. In the broader Cu-Nb-S system, there are two ternary phases; Cu_3NbS_4 and $Cu_{0.7}NbS_2$, which are characterized by Van Arkel & Crevecoeur [43].

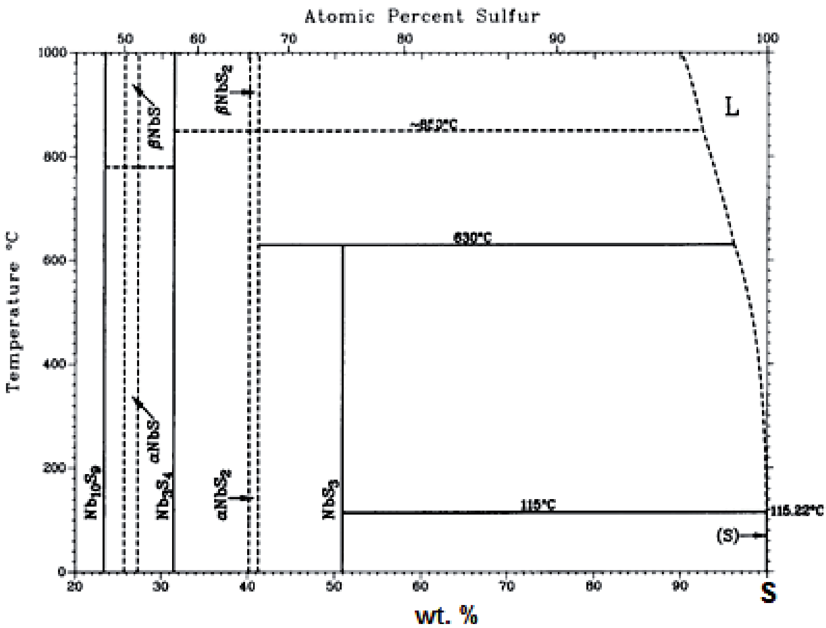

Figure 10. The Nb-S phase diagram [12]. Melting points of the intermediate phases are largely unknown.

3 Thermochemical Data

Earlier, Craig & Barton [7], Craig & Lee [8] and Lynch [44] compiled preliminary estimates and experimental data on the thermodynamic properties of sulfides, arsenides, sulfosalts, some of them are also included in Table 4. The former authors have also estimated the Gibbs energies for sulfidation reactions of sulfides and sulfosalts. The thermochemical data could be used in the prediction of the general behavior of sulfosalts and the stabilities in dry systems, as well as in improving procedures for extraction and refining of valuable metals from sulfide ores [7]. However, the data may not be sufficiently precise to predict the detailed structures of the complex phase diagrams.

The basic elemental and sulfide data on which the sulfosalt calculations are based have been documented and the assumptions are straight forward. In this study, we present a selective compilation of the Gibbs energies of formation data for some phases and sulfidation reactions which are of interest in the pyrometallurgy of Cu and Ni.

Equations for some of the Gibbs energies of formations and reactions were obtained by linear fitting and extrapolation of experimental data, within the temperature ranges of phase stabilities.

Table 4. Compilation of experimentally determined and estimated thermodynamic data of stable phases and phase assemblages in the Ni-(As, Se)-S and Cu-(As, Bi, Pb, Sb, Se, Te, Nb, Zn, Mo)-S systems. Standard states: S_2(g), As(s), Sb(s), Pb(s), Cu(s), Ni(s), Mo(s), Se(s,l), and Zn(s). The Gibbs energies of formation of all reactions are calculated or determined as written.

Reaction	$\Delta G_{T(K)}$ (J/mol)	T(K)	Ref.	Remarks
Ni-As-Se-S				
As(s) = As(l)	23645 - 21.7·T	1098	[45]	experimental
As(s) = As(g)	287997 - 157.1·T + 5.901·T·logT + $2.626\cdot10^{-3}\cdot T^2$	298- 1600	[47]	
2As(s) = As_2(g)	193580 - 244.3·T + 24.88·T·logT + $4.670\cdot10^{-3}\cdot T^2$	298- 1600		
3As(s) = As_3(g)	219490 - 272.8T + 22.64 ·T·logT + $7.027\cdot(10^{-3})\cdot T^2$	298- 1600		
4As(s) = As_4(g)	160700 - 279.8·T + 31.07·T·logT + $9.317\cdot10^{-3}\cdot T^2$	298 - 1600		
2As(s) + $\frac{3}{2}S_2$(g) = As_2S_3(s, l)	-291.52 - 0.021·T·lnT + $0.235\cdot(10^{-6})\cdot T^2$ + $116.29\cdot T^{-1}$ + 0.39·T	298 - 4585	[57]	
4As(s) + $3S_2$(g) = $2As_2S_3$(l)	-491870 + 428·T	585 – 718	[48]	
4As(s) + $2S_2$(g) = As_4S_4(l)	-350650 + 270·T	580 – 718		
$2As_2$(g) + $3S_2$(g) = As_4S_4(g)	-622920 + 461·T	298–1000		
As_2(g) + S_2(g) = 2AsS(g)	36410 - 22.2·T	298 – 1000	[49]	experimental
As + Ni = NiAs(s)	-73363 + 17.3·T	298 – 800	[45, 50]	
Ni(s) + ¼As_4(g) + ½S2(g) = NiAsS	-121000 + 54.7·T	825 - 975	[51]	
¼As4(g) + NiS(s) = NiAsS	-36750 + 39.5·T	684 - 810	[52]	NiS contained several wt. % NiAs
2As(s) + 3Se(s) = As_2Se_3 (s)	-86.1 ± 4.1 - (0.99)·T	298 - 400	-	determined from the data of [18]. 633 K is melting T.
2As(s) + 3Se(s) = As_2Se_3 (s)	- 92192 - 7.6308·T	500 - 633	-	
Ni + ½S_2(g) = NiS	- 147800 + 73.3·T	780 – 1250	[53]	± 2500 (J/mol)
3Ni + S_2(g) = Ni_3S_2	- 279470 + 102.8·T	845 – 1040	[53]	± 6000 (J/mol)
4Ni + $\frac{3}{2}S_2$(g) = Ni_4S_3	-435750 + 180.2·T	845 – 1040	[53]	± 8500 (J/mol)
Ni + S_2(g) = NiS_2	-257010 + 170.3·T	675 – 1070	[54]	± 3000 (J/mol)

Table 4. - (Continued.)

Cu-As-Bi-Pb-Sb-Se-Te-Nb-Zn-Mo-S				
$4As(s) + 3Cu(s) = Cu_3As\ (s)$	-108480 + 1.4·T	298 – 1098	[45, 50]	
$As_4(g) + 6Zn(l) = 2Zn_3As_2(s)$	-271960 – 346·T + 144·T·logT	613 – 853	[55]	
$5Mo + 2As_2(g) = Mo_5As_4$	-702980 + 537.4·T – 61.2·T·logT	298 - 2110	[56]	
$4Mo_5As_4(s) + 7As(g) = 10Mo_2As_3(s)$	-1913500 + 1882·T – 214.3·T· logT	298 – 1520	[56]	
$4Mo_2As_3(s) + As_4(g) = 8MoAs_2(s)$	-321600 + 595·T – 115·T· logT	298 - 1340	[56]	
$Cu + Te = Cu_2Te$	-(38100 ± 2900) - 4.03·T	298 - ?	-	determined from the data of [46]
$Cu + Te = Cu_4Te_3$	-(100000 ± 5400) + 8.39·T	298 - ?	-	determined from the data of [46]
$Cu + Te = CuTe$	-(23400 ± 3300) -4.36·T	298 - ?	-	determined from the data of [46]
$Nb(s) + S(s, l) = NbS(g)$	425120 -165.63·T	298 - 717	-	estimated from the data of [57]
$Nb(s) +0.5\ S_2(g) = NbS(g)$	361720 - 89.517·T	298 - 2000	-	estimated from the data of [57]
$Nb + S_2(g) = NbS_2$	-447903.864 + 159.18·T	1123 - 1373	[58]	± 5442.84
$Mo + S(s,l) = MoS_2(s)$	- 282942 + 48.912·T	298 - 717	-	estimated from the data of [57]
$Mo(s) + S_2(g) = MoS_2(s)$	- 398305 + 180.76·T	298 - 2000	-	estimated from the data of [57]
$2Mo(s) + 3S(s,l) = Mo_2S_3(s)$	- 416943 + 65.565·T	298 - 717	-	estimated from the data of [57]
$2Mo(s) + 1.5S(g) = Mo_2S_3(s,l)$	- 586600 + 257.6·T	298 - 2140	-	estimated from the data of [57]
$3Cu + As + 2S_2(g) = Cu_3AsS_4$ (Luzonite)	-437344.8 + 235.13·T	298-873	[59]	effect of transition neglected.
$3Cu + As + 2S_2(g) = Cu_3AsS_4$ (Enargite)	-437344.8 + 235.13·T	298-873	[59, 60]	effect of transition neglected.
$\frac{2}{3}Cu_{12}As_4S_{13} + S_2(g) = \frac{8}{3}Cu_3AsS_4$	-174070.4 + 146.1612·T	298 - 773	[59, 60]	
$12Cu + 4As + \frac{13}{2}S_2(g) = Cu_{12}As_4S_{13}$ (Tennantite)	-1488273.442 + 721.302·T	298-873	[59]	composition not well represented by formula

Table 4. - (Continued.)

$6Cu + 4As + \frac{9}{2}S_2(g) = Cu_6As_4S_9$ (Sinnerite)	-989508.312 + 572.8798·T	298-762	[59]	
$9Pb + 4As + \frac{15}{2}S_2(g) = Pb_9As_4S_{15}$ (Gratonite)	- 1990446.59 + 1047.91·T	298-523	[61]	effect of transition neglected
$3PbS + \frac{4}{3}As + S_2(g) = \frac{1}{3}Pb_9As_4S_{15}$	-192592.8 + 132.76·T	298 - 773	[7]	
$2Pb + 2As + \frac{5}{2}S_2(g) = Pb_2As_2S_5$ (Dufrenoyesite)	-602815.46 + 360.32·T	298-758	[61]	
$\frac{4}{5}Pb_9As_4S_{15} + 4AsS + S_2(g) = \frac{18}{5}Pb_2As_2S_5$	- 175008.2 + 115.51·T	298 - 554	[7]	
$\frac{4}{5}Pb_9As_4S_{15} + 4(S\text{-}As)_{(liq.)} + S_2(g) = \frac{18}{5}Pb_2As_2S_5$	-191755.44 + 139.8·T	281 - 723	[7]	
$3Pb + 4As + \frac{9}{2}S_2(g) = Pb_3As_4S_9$ (Baumhauerite)	-960745 + 658.42·T	298 - 773	[7]	
$6Pb_2As_2S_5 + 4AsS + S_2(g) = 4Pb_3As_4S_9$	-175008.24 + 128.45·T	298 - 554	[7]	
$6Pb_2As_2S_5 + 4(S\text{-}As)_{(liq.)} + S_2(g) = 4Pb_3As_4S_9$	-191755.44 + 152.74·T	554 - 873	[7]	
$Pb + 2As + 2S_2(g) = PbAs_2S_4$ (Sartorite)	-445852.33 + 299.27·T	298 - ?	[7]	formula uncertain
$13Pb + 18As + 20S_2(g) = Pb_{13}As_{18}S_{40}$ (Rathite I)	-4640523.52 + 2932.35·T	298 - ?	[7]	formula uncertain
$9Pb + 13As + 14S_2(g) = Pb_9As_{13}S_{28}$ (Rathite II)	-3246695.9 + 2018.04·T	298 - ?	[7]	formula uncertain
$Cu + Pb + As + \frac{3}{2}S_2(g) = CuPbAsS_3$ (Seligmannite)	-370029.38 + 191.25·T	298 - 600	[62]	
$Cu + Pb + As + \frac{3}{2}S_2(g) = CuPbAsS_3$ (Seligmannite)	-374844.2 + 205.57·T	600 - 733	[62]	
$\frac{2}{3}Cu_2S + \frac{4}{3}PbS + \frac{4}{3}As + S_2(g) = CuPbAsS_3$	-374844.2 + 129.67·T	298 - 377	[7]	
$\frac{2}{3}Cu_2S + \frac{4}{3}PbS + \frac{4}{3}As + S_2(g) = CuPbAsS_3$	-193484.59 + 136.45·T	377 - 708	[7]	
$6Cu + 3Zn + 4As + 6S_2(g) = Cu_6Zn_3As_4S_{12}$ (Nowackiite)	-1760260.51 + 797.92·T	298 - ?	[7]	
$Cu_2S + ZnS + \frac{4}{3}As + S_2(g) = \frac{1}{3}Cu_6Zn_3As_4S_{12}$	- 192860.76 + 124.85·T	298 – 377	[7]	
$Cu_2S + ZnS + \frac{4}{3}As + S_2(g) = \frac{1}{3}Cu_6Zn_3As_4S_{12}$	-196712.61 + 135.07·T	377 - ?	[7]	

Table 4. - (Continued.)

$10Cu + 2Zn + 4As + \frac{13}{2}S_2(g) =$ $Cu_{10}Zn_2As_4S_{13}$ (Zn-tennantite)	-2119070 + 908.3·T	298 – 693	[63]	
$10Cu + 2Zn + 4As + \frac{13}{2}S_2(g) =$ $Cu_{10}Zn_2As_4S_{13}$ (Zn-tennantite)	-2130050 + 923.9·T	693 -875	[63]	
$10Cu + 2Zn + 4Sb + \frac{13}{2}S_2(g) =$ $Cu_{10}Zn_2Sb_4S_{13}$ (Zn-tetrahedrite)	-2058151 + 903.2·T	298 – 693	[63]	
$10Cu + 2Zn + 4Sb + \frac{13}{2}S_2(g) =$ $Cu_{10}Zn_2Sb_4S_{13}$ (Zn-tetrahedrite)	-2,069,130 + 918.9·T	693 – 903	[63]	
$17Pb + 8Sb + 8As + \frac{41}{2}S_2(g) =$ $Pb_{17}Sb_8As_8S_{41}(s)$	-5214100 + 2787·T	298-600	[7]	
$17Pb + 8Sb + 8As + \frac{41}{2}S_2(g) =$ $Pb_{17}Sb_8As_8S_{41}(s)$	-5295900 + 3030·T	600-?	[7]	
$16Pb + 9Sb + 9As + \frac{43}{2}S_2(g) =$ $Pb_{16}Sb_9As_9S_{43}(s)$	-5375600 + 2939·T	298-600	[7]	
$16Pb + 9Sb + 9As + \frac{43}{2}S_2(g) =$ $Pb_{16}Sb_9As_9S_{43}(s)$	-5452603 + 3169·T	600-?	[7]	
$17Pb + 11Sb + 11As + 25S_2(g) =$ $Pb_{17}Sb_{11}As_{11}S_{50}(s)$	-6169230 + 3853·T	298-600	[7]	
$17Pb + 11Sb + 11As + 25S_2(g) =$ $Pb_{17}Sb_{11}As_{11}S_{50}(s)$	-6251040 + 4097·T	600-?	[7]	
$12Pb + 5Sb + 5As + \frac{27}{2}S_2(g) =$ $Pb_{12}Sb_5As_5S_{27}(s)$	-3474570 + 2022·T	298-600	[7]	
$12Pb + 5Sb + 5As + \frac{27}{2}S_2(g) =$ $Pb_{12}Sb_5As_5S_{27}(s)$	-3532320 + 2194·T	600-?	[7]	
$2Pb + Sb + As + \frac{5}{2}S_2(g) =$ $Pb_2SbAsS_5(s)$	-632157 + 346.0·T	298-600	[7]	
$2Pb + Sb + As + \frac{5}{2}S_2(g) =$ $Pb_2SbAsS_5(s)$	-641782 + 423.5·T	600-?	[7]	
$5Pb + Sb + As + 4S_2(g) =$ $Pb_5SbAsS_8(s)$	-1102840 + 537.8·T	298-600	[7]	
$5Pb + Sb + As + 4S_2(g) =$ $Pb_5SbAsS_8(s)$	-1126910 + 609.3·T	600-?	[7]	
$9Cu + Bi + 3S_2(g) = Cu_9BiS_6$	-792146.75 + 309.78·T	673 - 923	[64]	
$3Cu + Bi + \frac{3}{2}S_2(g) = Cu_3BiS_3$	-369531.16 + 168.1·T	298 - 544	[64]	
$3Cu + Bi + \frac{3}{2}S_2(g) = Cu_3BiS_3$	-380416.84 + 188.07·T	544 – 783	[64]	
$Cu + Bi + S_2(g) = CuBiS_2$	-232287.85 + 129.62·T	298 - 544	[64]	
$Cu + Bi + S_2(g) = CuBiS_2$	-243047.93 + 149.59·T	544 - 758	[64]	
$3Cu + 5Bi + \frac{9}{2}S_2(g) = Cu_3Bi_5S_9$	-1078624.35 + 711.08·T	698 – 863	[64]	

Table 4. – (Continued.)

$Cu + 3Bi + \frac{5}{2}S_2(g) = CuBi_3S_5$	-592277.28 + 413.11·T	673 - 918	[64]	
$6Cu_2S + \frac{4}{3}Bi_{liq} + S_2(g) = \frac{4}{3}Cu_9BiS_6$	-266900.13 + 229.14T	708 - 923	[7]	
$2Cu_2S + \frac{4}{3}Bi + S_2(g) = \frac{4}{3}Cu_3BiS_3$	-218220.20 + 136.78·T	298 – 377	[7]	
$2Cu_2S + \frac{4}{3}Bi + S_2(g) = \frac{4}{3}Cu_3BiS_3$	-225923.92 + 157.21·T	377 – 544	[7]	
$2Cu_2S + \frac{4}{3}Bi_{liq} + S_2(g) = \frac{4}{3}Cu_3BiS_3$	-240439.55 + 183.84·T	544 – 708	[7]	
$\frac{2}{3}Cu_3BiS_3 + \frac{4}{3}Bi + S_2(g) = 2CuBiS_2$	-218220.20 + 147.17·T	298 – 544	[7]	
$\frac{2}{3}Cu_3BiS_3 + \frac{4}{3}Bi_{liq} + S_2(g) = 2CuBiS_2$	-185479.43 + 173.79·T	544 - 785	[7]	
$\frac{1}{3}Cu_3BiS_3 + \frac{4}{3}Bi_{liq} + S_2(g) = \frac{1}{3}Cu_3Bi_5S_9$	-232735.84 + 174.33·T	698 - 758	[7]	
$\frac{1}{3}Cu_3Bi_5S_9 + \frac{4}{3}Bi_{liq} + S_2(g) = CuBi_3S_5$	-232735.84 + 176.10·T	698 – 863	[7]	
$6Pb + 2Bi + \frac{9}{2}S_2(g) = Pb_6Bi_2S_9$	-1269111.19 + 644.09·T	298 – 544	[65, 66]	> 400 ^oC composition changes to $Pb_9Bi_4S_{15}$ [65]
$6Pb + 2Bi + \frac{9}{2}S_2(g) = Pb_6Bi_2S_9$	-1290882.55 + 684.08·T	544 – 600	[65, 66]	
$8Pb + 6Bi + \frac{17}{2}S_2(g) = Pb_8Bi_6S_{17}$	-2303016.33 + 1335.17·T	544 – 600	[65, 66]	
$8Pb + 6Bi + \frac{17}{2}S_2(g) = Pb_8Bi_6S_{17}$	-2341534.89 + 1449.67T	600 – 873	[65, 66]	
$2Pb + 2Bi + \frac{5}{2}S_2(g) = Pb_2Bi_2S_5$	-640839.98 + 365.01·T	298 – 544	[65, 66]	
$2Pb + 2Bi + \frac{5}{2}S_2(g) = Pb_2Bi_2S_5$	-662611.34 + 404.99·T	544 – 600	[65, 66]	
$Pb + 2Bi + 2S_2(g) = PbBi_2S_4$	-484295.53 + 299.77·T	298 – 544	[65, 66]	
$Pb + 2Bi + 2S_2(g) = PbBi_2S_4$	-506066.89 + 330.21·T	544 - 600	[65, 66]	
$Pb + 4Bi + \frac{7}{2}S_2(g) = PbBi_4S_7$	-859985.47 + 592.89·T	953 - 1003	[65, 66]	
$4PbS + \frac{4}{3}Bi + S_2(g) = \frac{2}{3}Pb_6Bi_2S_9$	-218220.20 + 140.68·T	298 - 544	[7]	
$4PbS + \frac{4}{3}Bi_{liq} + S_2(g) = \frac{2}{3}Pb_6Bi_2S_9$	-232735.84 + 167.05·T	544 - 873	[7]	
$\frac{8}{15}Pb_6Bi_2S_9 + \frac{4}{3}Bi_{liq} + S_2(g) = \frac{2}{5}Pb_8Bi_6S_{17}$	-232735.84 + 169.23·T	544 - 873	[7]	

Table 4. – (Continued.)

$\frac{2}{3}Pb_8Bi_6S_{17} + \frac{4}{3}Bi + S_2(g) = \frac{8}{3}Pb_2Bi_2S_5$	-217102.32 + 163.24·T	298 - 544	[7]	
$\frac{2}{3}Pb_8Bi_6S_{17} + \frac{4}{3}Bi_{liq} + S_2(g) = \frac{8}{3}Pb_2Bi_2S_5$	-231617.96 + 189.91·T	544 - 698	[7]	
$\frac{2}{3}Pb_2Bi_2S_5 + \frac{4}{3}Bi + S_2(g) = \frac{4}{3}PbBi_2S_4$	-218500.72 + 173.04·T	298 - 994	[7]	
$\frac{2}{3}Pb_2Bi_2S_5 + \frac{4}{3}Bi_{liq} + S_2(g) = \frac{4}{3}PbBi_2S_4$	-247531.99 + 196.95·T	544 - 698	[7]	
$\frac{2}{15}Pb_8Bi_6S_{17} + \frac{4}{3}Bi_{liq} + S_2(g) = \frac{16}{15}PbBi_2S_4$	-232735.84 + 174.21·T	698 - 873	[7]	
$\frac{2}{3}PbBi_2S_4 + \frac{4}{3}Bi_{liq} + S_2(g) = \frac{2}{3}PbBi_4S_7$	-250458.56 + 195.44·T	953 - 1003	[7]	
$Cu + Pb + Bi + \frac{3}{2}S_2(g) = CuPbBiS_3$	-389250.98 + 177.52·T	298 - 544	[67]	
$Cu + Pb + Bi + \frac{3}{2}S_2(g) = CuPbBiS_3$	-400136.66 + 197.49·T	544 - 600	[67]	
$2Cu + 2Pb + 4Bi + \frac{9}{2}S_2(g) = Cu_2Pb_2Bi_4S_9$	-1105825.99 + 566.89·T	298 - 544	[7]	
$2Cu + 2Pb + 4Bi + \frac{9}{2}S_2(g) = Cu_2Pb_2Bi_4S_9$	-1149586.42 + 646.86·T	544 - 600	[7]	
$Cu + Pb + 5Bi + \frac{9}{2}S_2(g) = CuPbBi_5S_9$	-1043915.78 + 612.78·T	298 - 544	[7]	
$Cu + Pb + 5Bi + \frac{9}{2}S_2(g) = CuPbBi_5S_9$	-1098344.18 + 712.72·T	544 - 600	[7]	
$2Cu + 5Pb + 5Bi + 14S_2(g) = Cu_2Pb_5Bi_5S_{14}$	-1783907.56 + 878.14·T	298 – 544	[7]	
$2Cu + 5Pb + 5Bi + 14S_2(g) = Cu_2Pb_5Bi_5S_{14}$	-1838335.96 + 978.08·T	544 – 600	[7]	
$\frac{2}{3}Cu_2S + \frac{4}{3}PbS + \frac{4}{3}Bi + S_2(g) = \frac{4}{3}CuPbBiS_3$	-218220.20 + 110.95·T	298 – 377	[7]	
$\frac{2}{3}Cu_2S + \frac{4}{3}PbS + \frac{4}{3}Bi + S_2(g) = \frac{4}{3}CuPbBiS_3$	-219111.99 + 118.11·T	377 – 544	[7]	
$\frac{2}{3}Cu_2S + \frac{4}{3}PbS + \frac{4}{3}Bi + S_2(g) = \frac{4}{3}CuPbBiS_3$	-233627.63 + 144.74·T	544 – 708	[7]	
$\frac{1}{3}Cu_2S + \frac{2}{3}PbS + \frac{4}{3}Bi + S_2(g) = \frac{1}{3}Cu2Pb_2Bi_4S_9$	-218220.20 + 84.36·T	298 – 377	[7]	
$\frac{1}{3}Cu_2S + \frac{2}{3}PbS + \frac{4}{3}Bi + S_2(g) = \frac{1}{3}Cu2Pb_2Bi_4S_9$	-219111.99 + 118.11·T	377 – 544	[7]	
$\frac{1}{3}Cu_2S + \frac{2}{3}PbS + \frac{4}{3}Bi_{liq} + S_2(g) = \frac{1}{3}Cu2Pb_2Bi_4S_9$	-234016.10 + 156.34·T	544 – 708	[7]	
$\frac{2}{15}Cu_2S + \frac{4}{15}PbS + \frac{4}{3}Bi + S_2(g) = \frac{4}{15}CuPbBi_5S_9$	-216934.86 + 134.52·T	298 – 377	[7]	

Table 4. – (Continued.)

$\frac{2}{15}Cu_2S + \frac{4}{15}PbS + \frac{4}{3}Bi + S_2(g) = \frac{4}{15}CuPbBi_5S_9$	-217441.46 + 135.90·T	377 – 544	[7]	
$\frac{2}{15}Cu_2S + \frac{4}{15}PbS + \frac{4}{3}Bi_{liq} + S_2(g) = \frac{4}{15}CuPbBi_5S_9$	-231957.09 + 162.49·T	544 – 708	[7]	
$\frac{1}{4}Cu_2S + \frac{5}{4}PbS + \frac{5}{4}Bi + S_2(g) = \frac{1}{4}Cu2Pb5Bi_5S_{14}$	-216717.14 + 118.40·T	298 – 377	[7]	
$\frac{1}{4}Cu_2S + \frac{5}{4}PbS + \frac{5}{4}Bi + S_2(g) = \frac{1}{4}Cu2Pb5Bi_5S_{14}$	-217680.11 + 120.96·T	377 – 544	[7]	
$3Pb + 2Sb + 3S_2(g) = Pb_3Sb_2S_6$	-833445.34 + 488.73·T	883 – 903	[68]	
$3Pb + 4Sb + \frac{11}{2}S_2(g) = Pb_5Sb_4S_{11}$	-1481038.63 + 809.43·T	298 – 600	[68]	
$5Pb + 4Sb + \frac{11}{2}S_2(g) = Pb_5Sb_4S_{11}$	-1505112.73 + 893.59·T	600 – 873	[68]	
$5Pb + 6Sb + 7S_2(g) = Pb_5Sb_6S_{14}$	-1853224.22 + 1131.15·T	698 – 876	[68]	
$6Pb + 10Sb + \frac{21}{2}S_2(g) = Pb_6Sb_{10}S_{21}$	-2682336.22 + 1613.38·T	298 – 600	[68]	Formula uncertain
$6Pb + 10Sb + \frac{21}{2}S_2(g) = Pb_6Sb_{10}S_{21}$	-2711225.14 + 1699.26·T	600 – 853	[68]	Formula uncertain
$Pb + 2Sb + 4S_2(g) = PbSb_2S_4$	-505074.62 + 310.20·T	298 – 600	[68]	Formula uncertain
$Pb + 2Sb + 2S_2(g) = PbSb_2S_4$	-509889.44 + 328.71·T	600 – 818	[68]	Formula uncertain
$\frac{5}{3}PbS + \frac{4}{3}Sb + S_2(g) = \frac{1}{3}Pb_5Sb_4S_{11}$	-232074.32 + 153.70·T	298 – 883	[7]	
$\frac{2}{3}Pb_5Bi_4S_{11} + \frac{4}{3}Sb + S_2(g) = \frac{2}{3}Pb_5Sb_6S_{14}$	-232074.32 + 102.54·T	698 – 876	[7]	
$\frac{12}{39}Pb_5Bi_4S_{11} + \frac{4}{3}Sb + S_2(g) = \frac{10}{39}Pb_6Sb_{10}S_{21}$	-232074.32 + 160.77·T	298 – 698	[7]	
$\frac{2}{3}Pb_6Bi_{10}S_{21} + \frac{4}{3}Sb + S_2(g) = 4PbSb_2S_4$	-232074.32 + 165.25·T	298 – 818	[7]	
$3Cu + Sb + \frac{3}{2}S_2(g) = Cu_3SbS_3$	-379922.79 + 170.65·T	298 – 881	[69]	
$Cu + Sb + S_2(g) = CuSbS_2$	-242679.49 + 130.04·T	298 – 826	[69]	
$3Cu + Sb + 2S_2(g) = Cu_3SbS_4$	-466957.99 + 244.05·T	298 – 900	[69]	
$12Cu + 4Sb + \frac{13}{2}S_2(g) = Cu_{12}Sb_4S_{13}$	-1606717.99 + 725.91·T	298 – 816	[69]	composition not well represented

Table 4. – (Continued.)

$\frac{2}{3}Cu_2S + \frac{4}{3}Sb + S_2(g) = \frac{4}{3}Cu_3SbS_3$	-232078.51 + 140.22·T	298 – 377	[7]	
$\frac{2}{3}Cu_2S + \frac{4}{3}Sb + S_2(g) = \frac{4}{3}Cu_3SbS_3$	-239782.22 + 160.65·T	377 – 708	[7]	
$\frac{4}{3}Cu_3SbS_3 + \frac{4}{3}Sb + S_2(g) = 2CuSbS_2$	-232078.51 + 146.33·T	298 – 816	[7]	
$2Cu_3SbS_3 + S_2(g) = 2Cu_3SbS_4$	-174053.65 + 159.52·T	298 – 861	[7]	
$8Cu_3SbS_3 + S_2(g) = 2Cu_{12}Sb_4S_{13}$	-174053.65 + 137.50·T	298 – 813	[7]	
$Cu + Pb + Sb + \frac{3}{2}S_2(g) = CuPbSbS_3$	-399642.62 + 192.43·T	298 – 600	[7]	
$Cu + Pb + Sb + \frac{3}{2}S_2(g) = CuPbSbS_3$	-404457.44 + 206.74·T	600 - ?	[7]	
$Cu + 13Pb + 7Sb + 12S_2(g) = CuPb_{13}Sb_7S_{24}$	-3327534.66 + 1656.09·T	298 – 600	[7]	
$Cu + 13Pb + 7Sb + 12S_2(g) = CuPb_{13}Sb_7S_{24}$	-3390127.32 + 1842.19·T	600 - ?	[7]	
$\frac{2}{3}Cu_2S + \frac{4}{3}PbS + \frac{4}{3}Sb + S_2(g) = CuPbSbS_3$	-232078.51 + 131.21·T	298 – 377	[7]	
$\frac{2}{3}Cu_2S + \frac{4}{3}PbS + \frac{4}{3}Sb + S_2(g) = CuPbSbS_3$	-233137.77 + 137.10·T	377 – 708	[7]	
$\frac{2}{3}Cu_2S + \frac{4}{3}PbS + \frac{4}{3}Sb + S_2(g) = CuPbSbS_3$	-236039.22 + 139.88·T	708 - ?	[7]	
$\frac{2}{21}Cu_2S + \frac{51}{21}PbS + \frac{4}{3}Sb + S_2(g) = CuPb_{13}Sb_7S_{24}$	-232074.32 + 132.55·T	298 – 377	[7]	
$\frac{2}{21}Cu_2S + \frac{51}{21}PbS + \frac{4}{3}Sb + S_2(g) = CuPb_{13}Sb_7S_{24}$	-232442.76 + 133.52·T	377 – 708	[7]	

4 Discussion

Craig and Barton [7] derived approximate temperature dependent Gibbs energies of formations for a large number of sulfosalts, based on an assumption of near –ideal mixing of the simple sulfide end members to produce sulfosalts of intermediate composition, as expressed in Equation (1).

$$\Delta_f G_m^0(\text{sulfosalt, J/mol}) = [\textstyle\sum_1^n (N_1 \Delta_f G_m^0(\text{sulfide}) + .. N_i \Delta_f G_m^0(\text{sulfide}))] + (5.02 \pm 3.35) \cdot (R \cdot T(K) \cdot \textstyle\sum N_i \ln N_i), \quad (1)$$

where N_i is mole fraction of a component sulfide in the formation reaction. Their approach is based on the experimental work of [8], who found that an average value of the Gibbs energies of mixing (ΔG_{mix}) of reactions from the end-member sulfides for more than 20 different sulfosalts were very small, about -1884.06 + 1465.38 J/equivalent. In their estimates of ΔG_{mix}, they assumed $\Delta H_{mix}^o = 0$ and

$$\Delta S_{mix}^o = (5.02 \pm 3.35) \cdot (R \cdot T(K) \cdot \textstyle\sum N_i ln\, N_i). \quad (2)$$

In the absence of enthalpy data for sulfosalts their ideal mixing model did not include a heat of mixing term, though as they also noted that the heat of mixing needs not to be zero.

In fact, our experimental results on the Gibbs energies of formation of $AgBi_3S_5$ (pavonite) [70] have enabled us to assess the Craig and Barton's model quantitatively. Based on our enthalpy data for the formation of $AgBi_3S_5$ (pavonite) from the pure elements at their standard state (Equation (3)) the assumption of zero enthalpy of mixing made by Craig and Barton [7] (Equation (4)) may be a reasonable approximation.

- 234.99 + 0.0041·T (K) (299 – 460 K, kJ/mol) (3)

- 232.04 + (0.00165 ± 0.00175) ·T (K) (298 – 460 K, kJ/mol) (4)

In Table 4, not all sulfidation reactions are known to represent stable equilibria, such data are marked by the word 'uncertain formula'. Equations for some of the Gibbs energies of formations and reactions were obtained by linear fitting and extrapolation of experimental data, within the temperature ranges of phase stabilities.

Thermal stabilities of some pure sulfides and sulfosalts in the Cu-(As, Bi, Pb, Sb, Se, Te, Nb, Zn, Mo)-S and Ni-(As, Se)-S systems are also reviewed and compiled in an organized manner (see Appendix).

5 Summary and Conclusions

Thermodynamic properties of some equilibrium phases in the Ni-(As, Se)-S and Cu-(As, Bi, Pb, Sb, Se, Te, Nb, Zn, Mo)-S systems were compiled and reviewed, based on available literature. Particular emphasis was given to the compilation and refining of data for the standard Gibbs energies of formations of equilibrium phases which are of interest in the pyrometallurgy of copper and nickel production. Phase stabilities, phase relations and solubility limits of some equilibrium phases in the Ni-(As, Se)-S and Cu-Mo-Bi-Nb-S systems were reviewed. Thermal stabilities of some pure sulfides and sulfosalts (including the previous studies) were also compiled (see Appendix).

Experimental thermochemical data of the ternary and quaternary sulfidic phases are rare or unavailable in the literature. Thermochemical data of most binary sulfides in the multi-component systems are relatively well established. Gibbs energies of formations of some binary and ternary phases, mostly as a sulfidation reaction, have been reviewed and collected in Table 4.

Earlier reports [3, 5, 6] are also reviewed, updated, and extended, whenever necessary. The Gibbs energies of formations and reactions are mostly presented as linear equations, in each temperature ranges of phase stabilities.

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Appendix

Summary of some studies on the thermal stabilities (T_{max}) of sulfides and sulfosalts, at 1 atm., in the Cu-As-Bi-Pb-Sb-Se-Te-Nb-Zn-Mo-S and Ni-As-Se-S systems.

System	Chemical formula (mineral name)	T_{max} (°C)	Ref.
Pb-As-S	αAsS (realgar) βAsS	0 - 266 266 - 319 ± 2	[71, 72, 73, 74]
	As_2S_3 (orpiment)	310 ± 2	
	αAs_4S_3 (dimorphite) βAs_4S_3 γAs_4S_3	0 - 131 131 - 151 151 - 212 ± 2	
	PbS (galena)	1115	[75]
	$Pb_9As_4S_{15}$ (Gratonite)	250	[76, 77, 78, 79,80]
	$Pb_9As_4S_{15}$ (Jordanite)	549	
	$Pb_2As_2S_5$ (Dufrenoysite)	485 ?	
	$Pb_{19}As_{26}S_{58}$ (Rathite II)	474	
	$PbAs_2S_4$(Sartorite)	305	
	$Pb_3As_4S_9$(Baumhauerite)	458	[77]
Cu-As-S	Cu_2S / monoclinic (chalcocite)	103	[81]
	Cu_2S / hexagonal	103 -~435	
	Cu_2S / cubic	~435 - 1129	
	Cu_2S / tetragonal	> 1 Kbar	
	$Cu_{1.8+x}S$ / cubic (high digenite)	83 - 1129	
	$Cu_{1.97}S$ / orthorhombic (djurleite)	93	
	$Cu_{1.8}S$ / cubic (digenite)	76 - 83	
	$Cu_{1.78}S$ / monoclinic (roxbyite)	-	
	$Cu_{1.75}S$ / orthorhombic (anilite)	76	
	$Cu_{1.60}S$ /cubic (geerite)	-	
	$Cu_{1.4}S$ / hexagonal-R (spionkopite)	-	
	Cu_9S_8 / hexagonal-R (yarrowite)	up to 157	
	CuS /hexagonal-R (covellite)	up to 507	
	CuS_2/cubic (villamaninite)	-	
	Cu_3AsS_4 (Luzonite)	275 – 320	[59, 82]
	Cu_3AsS_4 (Enargite)	671	
	$Cu_{24}As_{12}S_{31}$ (-)	578	
	$Cu_6As_4S_9$ (Sinnerite)	489	
	$Cu_{12}AsS_{13}$ (Tennantite)	665	
	CuAsS (Lautite)	574	
	Cu_3AsS_3 (near- Tennantite) (-)	656	[83]
	$Cu_{12\pm x}AsS_{13\pm x}$ (Tennantite)	656	[84]

- (Continued.)

Ni-As-S	NiAsS (gersdorffite)	above 700	[72, 85]
Cu-Pb-S	$Cu_{14}Pb_2S_{9-x}$ (0 < x < 0.15)	486 - 528	[86, 87, 88]
Cu-Sb-S	Sb_2S_3 (stibnite)	550	[89]
	Cu_3SbS_4 (famatinite)	627 ± 2	[69, 90]
	$CuSbS_2$ (chalcostibnite)	553 ± 2	
	$Cu_{12+x}Sb_{4+y}S_{13}$	543	
	Cu_3SbS_3 (skinnerite, low T(mon.)) → Cu_3SbS_3 (skinnerite, high T(orth.))	122 ± 3	
	Cu_3SbS_3 (skinnerite)	607.5 ± 3	
Sb-As-S	$AsSbS_3$ (getchellite) $As_{0.98}Sb_{1.02}S_{3.00}$ (getchellite)	345	[66, 93, 94, 95, 96, 99]
	$(As, Sb)_{11}S_{18}$ (wakabayashilite)		
	$AsSb_2S_2$ (pääkkönenite)	538	
Cu-Zn-S	ZnS (sphalerite, sph) ZnS (wurtzite, wurt)	1185 (sublimation) 1830 (congruent at 3.7 atm) 1013 – 1130 (sph to wurt inversion based on the amount of S)	[81]
	Cu_3ZnS_4	< 200 ?	[86]
Cu-Nb-S	$Nb_{14}S_5$	1500	[12,35,40,41,42]
	$Nb_{21}S_8$	-	
	$Nb_{10}S_9$	-	
	αNbS	-	
	βNbS	-	
	Nb_3S_4	-	
	αNbS_2	-	
	βNbS_2	-	
	αNbS_3	0 - 630	
	Cu_3NbS_4	-	[43]
	$Cu_{0.7}NbS_2$	-	
Cu-Mo-S	MoS_2 (molybdenite)	1750 ± 50	[12]
	Mo_2S_3	~ 1800	
	$\sim CuMo_2S_3$	594– (> 1000)	[30]
Mo-Bi-S	Bi_2S_3 (bismuthinite)	25 - 775	[91]

- (Continued.)

Cu-Bi-S	Cu_9BiS_6 (-)	400 - 650	[64, 81]
	Cu_3BiS_3 (wittichenite)	25 - 510	
	$CuBiS_2$ (cuprobismutite)	25 - 485	
	$Cu_3Bi_3S_7$ (-)	~498	
	$Cu_3Bi_5S_9$	425 – 590	
	$CuBi_3S_5$	400 – 645	
	$Cu_{24}Bi_{26}S_{51}$ (emplectite → cuprobismutite)	319 ± 2 - 474 ± 5	[92]
Pb-Bi-S	$Pb_6Bi_2S_9$ (heyrovskyite) (> 400 °C composition changes to $Pb_9Bi_4S_{15}$ [65])	25 - 829	[65, 66, 76, 81]
	$Pb_8Bi_6S_{17}$ (-)	<400 - 816	
	$Pb_2Bi_2S_5$ (cosalite)	25 - 425	
	$PbBi_2S_4$ (galenobismutite)	25 - 750	
	$Pb_3Bi_2S_6$ (lillianite)	816	
	$PbBi_4S_7$ (bonchevite)	680 - 730	
	$Pb5Bi_4S_{11}$ (bursaite)	-	
	$PbBi_6S_{10}$ (ustarasite)	-	
Sb-Bi-S	$(Bi, Sb)_2S_3$ (horobetsuite)	> 200	[97, 98]
Bi-Se-S	$Bi_4(S,Se)_3$ (ikunolite)	-	[100, 101, 102]
Bi-Te-S	$Bi_2Te_{1.5+x}S_{1.5-x}$ (δ-tetradymite)	-	[103, 104, 105]
	$Bi_2Te_{2+x}S_{1-x}$ (β-tetradymite)	-	
	$Bi_8Te_7S_5$	-	
	$Bi_{18}(TeS_3)_3$ (joseite-C)	-	
	$Bi_9(Te_2S_2)$	-	
	$Bi_{15}(TeS_4)$	-	
Pb-Sb-S	$Pb_3Sb_2S_6$ (-)	610 – 642	[68]
	$Pb_5Sb_4S_{11}$ (boulangerite)	25 – 638	
	$Pb_5Sb_6S_{14}$ (-)	425 – 603	
	$Pb_6Sb_{10}S_{21}$ (robinsonite)	25 – 582	
	$PbSb_2S_4$ (zinckenite)	25 - 545	

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Due to increasing association of impurities in the copper and nickel ore minerals and concentrates, the production of high grade Cu and Ni by the conventional pyrometallurgical processes is compromised. Thus, smelters are in need to modify their operating flow sheets and strategies for processing more complex feed materials economically, while meeting the strict environmental regulations. To make the appropriate modifications, a thorough evaluation of the thermochemistry and thermal stabilities of phases and phase assemblages existing in these complex ore minerals is essential.

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