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Cite this article as:
Shuming Wen, Thermodynamic theory of flotation for a complex multiphase solid–liquid system and high-entropy flotation, *Int. J. Miner. Metall. Mater.*, 31(2024), No. 6, pp. 1177-1197. https://doi.org/10.1007/s12613-024-2874-z

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INTERNATIONAL JOURNAL OF
Minerals, Metallurgy and Materials

Volume 31, Number 6, June 2024
Page 1177

Research Article https://doi.org/10.1007/s12613-024-2874-z

Thermodynamic theory of flotation for a complex multiphase solid–liquid system and high-entropy flotation

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(Received: 7 December 2023; revised: 3 March 2024; accepted: 5 March 2024)

Abstract: The flotation of complex solid–liquid multiphase systems involve interactions among multiple components, the core problem facing flotation theory. Meanwhile, the combined use of multicomponent flotation reagents to improve mineral flotation has become an important issue in studies on the efficient use of refractory mineral resources. However, studying the flotation of complex solid–liquid systems is extremely difficult, and no systematic theory has been developed to date. In addition, the physical mechanism associated with combining reagents to improve the flotation effect has not been unified, which limits the development of flotation theory and the progress of flotation technology. In this study, we applied theoretical thermodynamics to a solid–liquid flotation system and used changes in the entropy and Gibbs free energy of the reagents adsorbed on the mineral surface to establish thermodynamic equilibrium equations that describe interactions among various material components while also introducing adsorption equilibrium constants for the flotation reagents adsorbed on the mineral surface. The homogenization effect on the mineral surface in pulp solution was determined using the chemical potentials of the material components of the various mineral surfaces required to maintain balance. The flotation effect can be improved through synergy among multicomponent flotation reagents; its physical essence is the thermodynamic law that as the number of components of flotation reagents on the mineral surface increases, the surface adsorption entropy change increases, and the Gibbs free energy change of adsorption decreases. According to the results obtained using flotation thermodynamics theory, we established high-entropy flotation theory and a technical method in which increasing the types of flotation reagents adsorbed on the mineral surface, increasing the adsorption entropy change of the flotation reagents, decreasing the Gibbs free energy change, and improving the adsorption efficiency and stability of the flotation reagents improves refractory mineral flotation.

Keywords: multicomponent flotation reagent; adsorption entropy change; equations of thermodynamic equilibrium; adsorption equilibrium constant; high-entropy flotation

1. Introduction

More than 100 years of development have led to considerable mineral flotation success. Mineral resources recovered through flotation have contributed substantially to the economic development of human society. The recovery of target minerals through flotation has achieved good technical and economic indicators for some highly floatable ores with simple mineral compositions. In addition, extensive experimental research using appropriate reagent systems and process flows has delivered good results for some poorly floatable ores with complex compositions. However, despite extensive experimental research, effective recycling has not yet been achieved for poorly floatable ores with similar target and gangue mineral floatabilities and complex mineral compositions. Indeed, mineral flotation technology has remained ahead of basic theory for over 100 years. Moreover, developed theories are mostly limited to qualitatively explaining process technology, with minimal theoretical guidance on flotation processes and reagent systems provided, which is an important reason why theoretical research in the flotation field has been highly valued, domestically and internationally, in recent decades. Solubility product theory relies on the concentration product of the constituent ions in an equilibrated solution system and is based on solution chemistry, in which flotation reagents more easily form precipitates when interacting with ions in the pulp solution when the solubility product is low, with flotation reagents with stronger adsorption capacities for the mineral surface leading to higher-stability adsorbates. However, the ions on mineral surfaces are constrained by other components, and their properties differ considerably from those in solution. The solubility product, a criterion for the adsorption capacity of a flotation agent on a mineral surface, can lead to considerable and sometimes severe errors.

The presence of numerous minerals, potentially dozens or hundreds, highly complicates flotation systems associated with actual ores. This complexity stems from the dissolution

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of the surface minerals, resulting in numerous substances in the pulp solution. In addition, the potential for numerous chemical reactions among these components makes the system more complicated and exceedingly challenging to navigate. Through flotation theory research, drawing precise conclusions for specific minerals and certain flotation reagents of such multifaceted systems is challenging and often leads to inadequate theoretical guidance or, at best, a constrained direction. Developing an understanding of the multiple interactions that occur between flotation reagents and minerals found in actual ores is arduous. Even when studied in depth, the equilibrium of a system formed by numerous minerals in a pulp solution differs markedly from that of a single-mineral system. Consequently, insight from theoretical research inadequately reflects the actual mineral flotation system. For recalcitrant ores, multiple flotation reagents are often added to enhance flotation effects. Such intricate flotation reagents further complicate the pulp solution and mineral surface, and contemporary theory fails to reflect the physical and chemical behavior of such intricate systems. Without systematic theoretical guidance, pragmatic flotation often relies on extensive experimental studies that are important for identifying suitable flotation reagent systems and process parameters. Consequently, mineral flotation is largely considered a technical practice that heavily depends on experimentation.

Rational reagent formulation is crucial for maximizing mineral flotation efficiency. Mineral flotation systems differ in appropriate reagent formulations for reference and adoption, which benefit from abundant production practice experience and extensive theoretical research. For example, depressants must be added to the chalcopyrite–molybdenite flotation separation system to reduce the floatability of chalcopyrite. Chalcopyrite depressants can be divided into sulfur- and cyanide-containing depressants based on differences in composition; the former mainly includes Na_2S as well as phosphorus (P_2S_5 + NaOH) and arsenic (As_2O_3 + Na_2S) Noke reagents, sodium thioglycolate, dithiocarbonate, and trithiocarbonate, while the latter mainly includes NaCN and KCN [1–8]. Although some reagents separate chalcopyrite and molybdenite well, they also have disadvantages, including high toxicities, dosages, and costs, as well as poor solubilities. Multicomponent depressants strongly inhibit chalcopyrite [9]. Combining organic depressants with inorganic depressants, inorganic depressants with inorganic depressants, or organic depressants with organic depressants has been shown to improve inhibitory performance. Yin *et al.* [10] studied the combination of disodium trithiocarbonate (DT), disodium carboxymethyl trithiocarbonate (DCMT), and the phosphorus Nokes reagent (PN), finding that the PN + DT + DCMT combination exhibited a better inhibitory effect than other depressant systems. In addition, according to Yin *et al.*, the combination of PN, sodium trithiocarbonate, and modified cyclodextrin effectively inhibits chalcopyrite to afford a molybdenum concentrate with high recovery [11]. Therefore, multicomponent depressants can exploit the complementary advantages of different depressants, which is an important developmental direction.

Galena is a typical lead sulfide mineral that is mainly associated with copper sulfide minerals (mainly chalcopyrite); hence, these two minerals are difficult to separate [12]. Given the superior floatability of chalcopyrite over galena, galena depressants are often added in production practices to separate the two minerals. Galena depressants are mainly divided into two categories: inorganic and organic depressants [13]. Commonly used inorganic depressants include dichromate, sulfite, phosphate, silicate, sodium cyanide, and sodium sulfide; these agents are widely available, inexpensive, and exhibit good inhibitory effects toward galena under suitable reaction conditions [14]. Agents such as dichromate and sodium cyanide are highly selective and widely applicable, but their high toxicity limits their industrial application [15]. Organic depressants have many advantages, including versatility, ease of control, and environmental friendliness; they are divided into large- and small-molecule organic depressants according to molecular weight. Common large-molecule organic depressants include carboxymethylcellulose, starch, dextrin, humate, lignin, and various plant gums [16]. Representative small-molecule organic depressants mainly include polyhydroxythiophosphates and polyhydroxyxanthates, composed of nitrogen- and phosphorus-containing prosoluble groups and hydrophilic groups. These compounds are considerably inhibitory toward galena at low doses [14]. Production practices and theoretical studies have shown that, in most cases, combined galena depressants are substantially more inhibitory than a single depressant while also reducing chemical consumption and providing certain economic benefits. Researchers studied the inhibitory effects of combinations of dichromate, dichromate + sodium sulfide, dichromate + water glass, and dichromate + carboxymethylcellulose on lead sulfide minerals and reported that a combination of galena depressants was more effective than dichromate alone [17–18]. Yu *et al.* [19] used sulfite + sodium sulfide + starch as a combination galena depressant to separate a mixed copper–lead concentrate from Lincang, Yunnan Province, China, and reported 20.41% copper in the copper concentrate with a copper recovery of 77.09% and 48.68% lead in the lead concentrate with a lead recovery of 97.73%, which are good separation indicators. Zhang *et al.* [20] studied the flotation behavior and electrochemical mechanism of galena and chalcopyrite under the single and combined uses of sodium silicate and sodium sulfite through microflotation testing and electrochemical measurements, and reported that the combined use of sodium silicate and sodium sulfite was more effective in inhibiting galena than the use of sodium silicate or sodium sulfite alone, with the chalcopyrite maintaining good hydrophobicity. Electrochemical measurements showed that more hydrophilic substances were produced on the surface of galena through simultaneous interactions with sodium silicate and sodium sulfite, which greatly weakened collector adsorption on this surface, thereby effectively inhibiting galena flotation and delivering copper–lead separation.

The combined use of different flotation collectors during zinc oxide ore flotation has attracted increasing research interest [21–23]. Wu *et al*. [24] reported the effective recovery and use of ZnO ore using amyl xanthate and dithiophosphate as a combined collector and sodium sulfide and copper sulfate as a sulfidizing agent and activator, respectively. Wang *et al*. [25] discovered that sodium oleate and dodecylamine are co-adsorbed on a smithsonite surface. By mixing benzohydroxamic acid (BHA) with sodium oleate (NaOL), Wang *et al*. [26] prepared BHOA, a new composite collector, and used it to flotation separate smithsonite and dolomite. Good flotation separation results were obtained at BHA/NaOL molar ratio of 2:1. Mehdilo *et al*. [27] examined the effects of combining Armac C and Armac T with pentylxanthate, finding that the Armac-T/pentyl-xanthate combination exhibited higher selectivity, whereas the Armac-C/pentyl-xanthate combination exhibited better collection performance. Hosseini and Forssberg [28] investigated the isoamyl xanthate/dodecylamine combination collector system and found that the electrostatic attraction between the xanthate and dodecylamine enhances the propensity for hydrophobic clustering of both molecules.

Common multicomponent flotation reagents for scheelite flotation include mixed anionic collectors, anionic–cationic collector combinations, and anionic–nonionic collector combinations [29–33]. However, scheelite activation often uses a single ion, with lead ions improving flotation recovery by adsorbing collectors such as hydroxamic acid and sodium oleate onto the scheelite surface [34–35]. The combination of lead ions and the BHA chelate enhances the flotation recovery of scheelite more than the separate use of these two reagents [36]. Adding a trace amount of NaOL as a promoter to the lead-ion/benzohydroxamic acid system produces Pb–BHA–NaOL, which improves the scheelite flotation index [37]. BHA/sodium dodecyl sulfate (SDS) coordination to lead ions considerably improves the collection capacity of lead BHA, reducing the amount of lead ions and BHA required by 30% [38]. Moreover, iron ions and the BHA chelate improve scheelite floatability [39], while Mn ions increase the adsorption capacity of BHA on the scheelite surface and enhance its floatability [40].

Salicylhydroxamic acid, BHA, styrene phosphoric acid, benzylarsonic acid, and sodium oleate were mainly used as collectors to float fine-grained cassiterite [41–42]. However, metal-ion activation is often required to improve surface activity when these collectors are used alone [43]. The addition of metal ions has shortcomings, such as the consumption of numerous mineral processing agents and excessive heavy metals in the water returned following mineral processing [44]. Many researchers have recently reported collector combination methods for optimizing mineral separation [45–47]. Currently, mechanisms that exploit mixed collector synergy mainly include co-adsorption, functional complementation, and charge compensation [48–49]. Co-adsorption is a commonly used mechanism. Miao *et al*. [50] found that NaOL and SHA co-adsorb on the surface of cassiterite, increasing the adsorption density of the collector on this surface.

The rational combined use of multicomponent flotation reagents can improve the flotation effect, with current theoretical research attributing this improvement to synergy and co-adsorption. However, these attributes do not reflect their physical or chemical nature. Therefore, the mechanism that underpins synergy between multicomponent flotation reagents must be further explored and studied.

During actual flotation, the surfaces of various mineral particles are oxidized and dissolved in an aqueous solution through the action of water molecules, with the fluid inclusion components in the mineral crystals released to the aqueous solution and flotation reagents added. Numerous material components are present in the slurry solution, and various chemical interactions between them establish a chemical equilibrium based on thermodynamic laws. An aqueous system has the lowest free energy and thermodynamic stability when in chemical equilibrium. At the same time, the surfaces of the various mineral particles in a pulp solution interact with the material components and various flotation reagents. Moreover, physical and chemical processes, such as the adsorption and desorption of material components or flotation reagents on the mineral surface, change the chemical composition and material structure of this surface. Although such changes cannot be fundamentally explained by flotation theories, such as solubility product theory, electric double-layer theory, and adsorption theory, the laws of physics nevertheless govern these changes. Therefore, we rely on the second law of thermodynamics, in which spontaneous processes in isolated systems always increase entropy and decrease Gibbs free energy. Accordingly, we conducted an in-depth thermodynamic study of complex systems composed of single and multiple minerals. Constructing a preliminary theoretical thermodynamic framework that reveals the thermodynamic laws that drive complex flotation systems is important for understanding and guiding the flotation of actual ores.

2. Thermodynamic basis of mineral flotation

From a thermodynamics perspective, an entire actual mineral flotation system includes gas, solid, and liquid phases. Gas bubbles are often omitted from studies that examine interactions between agents and mineral surfaces; therefore, we mainly considered the solid–liquid pulp solution system, in which water and aqueous-phase substances constitute a homogeneous liquid phase in addition to the different types of solid mineral particles. We consider this aqueous solution a single-phase multicomponent system (i.e., a subsystem of the solid–liquid flotation system). Different minerals have different physicochemical properties; however, the internal regions of mineral particles do not participate physicochemically during flotation. The surfaces of mineral particles are the relevant regions that we consider when studying flotation behavior; therefore, the surface region of a mineral particle can be treated as a flotation subsystem. Different mineral particle surface regions contribute differently to flotation subsystems. Thus, a solid–liquid mineral flotation system comprises an aqueous solution subsystem and multiple mineral surface subsystems. A graduated component concentration always arises at the solid–liquid interface during flotation; that is, the solid–liquid interface region is a nonuniform system but very small compared to the entire solid–liquid system. Hence, the research process can be simplified by ignoring this nonuniformity and treating the pulp–solution subsystem and various mineral surface subsystems as homogeneous.

2.1. Thermodynamic functions of solid–liquid flotation systems

Flotation is a physicochemical process that occurs at the solid–liquid interface. The amounts of material that dissolves from the solid mineral surface into the pulp solution, as well as the amounts of material that are artificially added as flotation agents, are minuscule compared to the content of the pulp solution. Therefore, the amount of heat produced by a solid–liquid system is usually small. Heat exchange between the exterior environment and the system can be ignored when the exterior temperature change is subtle; consequently, solid–liquid flotation systems can be considered isolated systems after flotation agents are added.

Thermodynamic state functions are physical quantities that depend only on the state of the system and not on the process that changes it; they include the enthalpy (H), internal energy (U), Helmholtz free energy (A), Gibbs free energy (G), entropy (S), temperature (T), pressure (p), and volume (V) for a solid–liquid flotation system, while heat (Q), work (W), and the amount of substance (n) in the system are process parameters. We often treat internal energy, enthalpy, Gibbs free energy, and entropy as important thermodynamic state functions and consider temperature, pressure, volume, and the amount of substance as system variables. The following four basic thermodynamic equations define the primary thermodynamic functions:

$$U = U(T, p, n) = Q + W \tag{1}$$

$$H = U + pV \tag{2}$$

$$S = \frac{Q}{T} \tag{3}$$

$$G = U - TS + pV \tag{4}$$

The state of the solid–liquid flotation system after adding flotation agents but before these agents interact with the mineral surface is referred to as “initial state 1.” The state of the system in which flotation agents interact with various mineral surfaces and reach equilibrium is referred to as “final state 2” (or the “thermodynamic equilibrium state”). Flotation thermodynamics neglects interactions between components, such as flotation agents; rather, it only considers initial state 1 and final state 2.

In initial state 1, the thermodynamic state functions of the system are expressed as

$$U_1 = U_1(T_1, p_1, n) \tag{5}$$

$$H_1 = U_1 + p_1V_1 \tag{6}$$

$$S_1 = \frac{Q_1}{T_1} \tag{7}$$

$$G_1 = U_1 - T_1S_1 + p_1V_1 \tag{8}$$

while in final state 2, these functions are expressed as

$$U_2 = U_2(T_2, p_2, n) \tag{9}$$

$$H_2 = U_2 + p_2V_2 \tag{10}$$

$$S_2 = \frac{Q_2}{T_2} \tag{11}$$

$$G_2 = U_2 - T_2S_2 + p_2V_2 \tag{12}$$

The changes in the thermodynamic state functions for the actions of equal flotation chemical material components are subsequently written as

$$\Delta U = U_2 - U_1 \tag{13}$$

$$\Delta H = H_2 - H_1 \tag{14}$$

$$\Delta S = S_2 - S_1 \tag{15}$$

$$\Delta G = G_2 - G_1 \tag{16}$$

Because the heat and work exchanged between the system and the environment can be neglected and the temperature, pressure, and volume of the system are constant, the amount of matter in the system is constant, indicationg the system is isolated with constant temperature, pressure, and volume. Therefore, the changes in temperature, pressure, and volume of the system are zero; that is:

$$\Delta U = \delta \mathrm{Q} \tag{17}$$

$$\Delta H = \delta \mathrm{Q} \tag{18}$$

$$\Delta S = \frac{\delta \mathrm{Q}}{T} \tag{19}$$

$$\Delta G = \Delta H - T\Delta S \tag{20}$$

where $\delta \mathrm{Q}$ is the heat effect associated with the action of the flotation agent, which is the heat change associated with the physicochemical flotation action.

Eqs. (17) and (20) are mathematical expressions of the first and second laws of thermodynamics for mineral flotation, respectively. Flotation agents are spontaneously adsorbed on the mineral surface in a solid–liquid flotation system. According to Eq. (20), a spontaneous process exhibits a negative Gibbs free energy change and a positive entropy change. Therefore, $\Delta G < 0$ and $\Delta S > 0$ for a solid–liquid flotation system in which flotation agents are spontaneously adsorbed on the mineral surface.

2.2. Partial molar quantities of thermodynamic functions

The thermodynamic functions of the material components also change with the material components of a system. Many types of material components are found in mineral flotation systems and belong to a typical complex multicomponent system. Because a multicomponent system contains more than one type of substance, the amount of each substance n_i is also a variable that determines the state of the system. The aqueous solution and various mineral surfaces constitute different subsystems in a solid–liquid mineral flotation system. Each subsystem can be treated as an open system when material components are exchanged between the pulp solution and various mineral surfaces, that is, when adsorption/desorption behavior occurs on a mineral surface. The thermodynamic functions of a multicomponent system with a variable number of internal components should also include n_i.

In thermodynamics, properties that remain constant as the amount of matter is changed are referred to as "intensive properties," which include temperature, density, and pressure. Properties that depend on the amount of matter are referred to as "extensive properties," which include internal energy, enthalpy, entropy, free energy, and volume. The partial molar quantity of a thermodynamic function is an intensive property and an important concept of a multicomponent system.

The value of a thermodynamic property of a homogeneous multicomponent slurry–solution system is not the sum of the values of that property for each pure component. For example, the volume of a two-component mixture may not equal the sum of the volumes of the pure substances. Consider a homogeneous system composed of components 1, 2, 3, …, k; accordingly, any extensive property Z of the system (V, G, S, U, H) depends on not only temperature and pressure but also the amount of each component in the system; that is, the number of moles n_1, n_2, n_3, …, n_k, which can be expressed in functional form as

$$Z = Z(T, p, n_1, n_2, n_3, \ldots, n_k) \tag{21}$$

If the temperature, pressure, and composition of the system change slightly, then the value of a certain extensive system property Z changes accordingly:

$$\mathrm{d}Z = \left(\frac{\partial Z}{\partial T}\right)_{p,n_1,n_2,n_3,\ldots,n_k}\mathrm{d}T + \left(\frac{\partial Z}{\partial p}\right)_{T,n_1,n_2,n_3,\ldots,n_k}\mathrm{d}p + \left(\frac{\partial Z}{\partial n_1}\right)_{T,p,n_2,n_3,\ldots,n_k}\mathrm{d}n_1 + \left(\frac{\partial Z}{\partial n_2}\right)_{T,p,n_1,n_3,\ldots,n_k}\mathrm{d}n_2 + \cdots + \left(\frac{\partial Z}{\partial n_k}\right)_{T,p,n_2,n_3,\ldots,n_{k-1}}\mathrm{d}n_k \tag{22}$$

At constant temperature and pressure, Eq. (22) can be written as

$$\mathrm{d}Z = \sum_{i=1}^{k}\left(\frac{\partial Z}{\partial n_i}\right)_{T,p,n_C(C\neq i)}\mathrm{d}n_i \tag{23}$$

We define Z_i as the partial molar quantity of component i for extensive property Z. Accordingly:

$$Z_i = \left(\frac{\partial Z}{\partial n_i}\right)_{T,p,n_C(C\neq i)} \tag{24}$$

Substituting Eq. (24) into Eq. (23) leads to

$$\mathrm{d}Z = \sum_{i=1}^{k} Z_i\mathrm{d}n_i \tag{25}$$

The partial molar quantity Z_i of a thermodynamic function has the following meaning: the change in the extensive thermodynamic property Z of the system caused by adding 1 mol of component i at constant temperature and pressure in a large system with the amounts of other components remaining constant (i.e., n_C is constant, where $C \neq i$). Alternatively, the thermodynamic extensive property of a finite system changes by dZ when dn_i is added, where $\mathrm{d}Z/\mathrm{d}n_i = Z_i$. Common partial molar quantities include partial molar volume V_i, partial molar internal energy U_i, partial molar enthalpy H_i, partial molar entropy S_i, partial molar Gibbs free energy G_i, and partial molar Helmholtz free energy A_i; their corresponding definitions are provided in Eq. (26):

$$\begin{cases} V_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_C(C\neq i)} \\ U_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,p,n_C(C\neq i)} \\ H_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,p,n_C(C\neq i)} \\ S_i = \left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_C(C\neq i)} \\ A_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,p,n_C(C\neq i)} \\ G_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_C(C\neq i)} \end{cases} \tag{26}$$

Any change in environmental temperature can be ignored in a solid–liquid flotation system while the pressure remains basically unchanged. Therefore, the partial molar quantity of a thermodynamic function of the system depends primarily on the types and amounts of substances in the system. Among the expressions in Eq. (26), S_i and G_i are more commonly used to study the chemical and phase equilibria of systems. Therefore, in a solid–liquid flotation system, S_i and G_i are thermodynamic quantities that need to be emphatically studied.

The partial molar quantity of a thermodynamic function is an intensive property independent of the amount of matter in the system. However, some thermodynamic functions exhibit extensive additive properties. Consequently, the thermodynamic function Z of the system can be obtained by integrating Eq. (25) when components n_1, n_2, n_3, ..., n_k, such as flotation agents, are added to the flotation system, or the mineral surface is dissolved by the solution, leading to:

$$Z = Z_1\int_0^{n_1}\mathrm{d}n_1 + \cdots + Z_k\int_0^{n_k}\mathrm{d}n_k = n_1 Z_1 + \cdots + n_k Z_k = \sum_{i=1}^{k} n_i Z_i \tag{27}$$

Eq. (28) holds true for thermodynamic functions because Z represents any extensive property of the system:

$$\begin{cases} V = \sum_{i=1}^{k} n_i V_i \\ U = \sum_{i=1}^{k} n_i U_i \\ H = \sum_{i=1}^{k} n_i H_i \\ S = \sum_{i=1}^{k} n_i S_i \\ A = \sum_{i=1}^{k} n_i A_i \\ G = \sum_{i=1}^{k} n_i G_i \end{cases} \tag{28}$$

Eq. (28) reveals that the partial molar quantities of the state functions of a thermodynamic system are not independent and must satisfy their additivity requirements.

2.3. Chemical potential of each component in a solid–liquid flotation system

A solid–liquid flotation system is a typical complex system whose components tend to change in amount through the adsorption/desorption of the solid mineral surfaces from/into the solution, the dissolution of the mineral surfaces, and other processes. The chemical potential, a physical quantity introduced by Gibbs and Lewis, can be used to study the thermodynamic relationships in open systems.

The system is no longer a standard homogeneous system after substances are adsorbed onto the surfaces of minerals. However, the system can roughly be treated as homogeneous, with the results obtained providing considerable guidance for mineral flotation. Any property of a mineral surface is a function of the amount of each substance and any two independent thermodynamic function variables, such as p, V, T, and U. The variable n_i should also be added to the basic thermodynamic equations.

(1) Thermodynamic energy.

Thermodynamic energy U is a property of capacity. If the system contains substances 1, 2, 3, ..., k, with amounts n_1, n_2, n_3, ..., n_k, respectively, then:

$U = U(S, V, n_1, n_2, n_3, \ldots, n_k)$, and its differential form is:

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} \mathrm{d}V + \sum\nolimits_{i=1}^{k} \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_C} \mathrm{d}n_i \quad (29)$$

where $\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_C}$ is defined as the chemical potential of substance i and is represented by the symbol μ_i. Accordingly:

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_C} \quad (30)$$

μ_i has the following physical meaning: $\mathrm{d}U$ is the change in the thermodynamic energy of the system if component i with $\mathrm{d}n_i$ is added to a system in which the entropy, volume, and the amounts of other components (n_C) remain unchanged; $\mathrm{d}U/\mathrm{d}n_i = \mu_i$.

According to the four basic thermodynamic equations, the following formula holds true for a system with constant composition:

$$\begin{cases} \left(\frac{\partial U}{\partial S}\right)_{V,n_i} = T \\ \left(\frac{\partial U}{\partial V}\right)_{S,n_i} = -p \end{cases} \quad (31)$$

Therefore, Eq. (29) can be written as

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum\nolimits_{i=1}^{k} \mu_i \mathrm{d}n_i \quad (32)$$

(2) Gibbs free energy.

From the mathematical expression of the second law of thermodynamics (Eq. (4)), which affords Eq. (33) through substitution with Eq. (32):

$$\mathrm{d}G = -S\,\mathrm{d}T + V\mathrm{d}p + \sum\nolimits_{i=1}^{k} \mu_i \mathrm{d}n_i \quad (33)$$

If T, p, n_1, n_2, n_3, …, n_k are independent variables, $G = G(T, p, n_1, n_2, n_3, ..., n_k)$ can be fully differentiated to:

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{p,n_i} \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_{T,n_i} \mathrm{d}p + \sum_{i=1}^{k} \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_C} \mathrm{d}n_i = -S\,\mathrm{d}T + V\mathrm{d}p + \sum_{i=1}^{k} \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_C} \mathrm{d}n_i,$$

which leads to the following equation by comparison with Eq. (33):

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_C} = \mu_i \quad (34)$$

Another expression for chemical potential can be obtained using the same method:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_C} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_C} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_C} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_C} \quad (35)$$

Eq. (35) shows that the partial derivatives of the four thermodynamic functions are chemical potentials, which broadly defines the chemical potential. Consequently, the four fundamental thermodynamic equations can be written as follows when the system components change:

$$\begin{cases} \mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum\limits_{i=1}^{k} \mu_i \mathrm{d}n_i \\ \mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \sum\limits_{i=1}^{k} \mu_i \mathrm{d}n_i \\ \mathrm{d}A = -S\,\mathrm{d}T - p\mathrm{d}V + \sum\limits_{i=1}^{k} \mu_i \mathrm{d}n_i \\ \mathrm{d}G = -S\,\mathrm{d}T + V\mathrm{d}p + \sum\limits_{i=1}^{k} \mu_i \mathrm{d}n_i \end{cases} \quad (36)$$

Physical or chemical processes occur under isothermal and isobaric conditions during actual mineral flotation production and laboratory testing. Therefore, using the chemical potential expressed in terms of partial molar Gibbs free energies is generally appropriate for studying solid–liquid flotation; that is $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_C}$. The Gibbs free energy of 1 mol of matter is the physical essence of the chemical potential under isothermal and isobaric conditions; this energy reflects the ability of the matter to perform physical and chemical actions. The chemical potential reflects the ability of a substance, such as a mineral surface component or flotation agent, to exert physical and chemical effects.

According to physicochemical theory, the chemical potential of substance i in a dilute solution is expressed as

$$\mu_i = \mu_i^0(T, p) + RT\ln x_i \quad (37)$$

where R is the gas constant, x_i is the mole fraction of substance i in solution, and $\mu_i^0(T, p)$ is the standard chemical potential of substance i, determined by the standard chemical potential of pure substance i and the properties of the system.

The mineral surface subsystem in a solid–liquid flotation system is not a dilute solution system; however, the chemical potential of substance i on a mineral surface can still be approximated by Eq. (37). At this time, standard chemical potential $\mu_i^0(T,p)$ of adsorbed substance i depends on the mineral surface; $\mu_i^0(T,p)$ is determined by the standard chemical potential of pure substance *i* and the adsorption properties of substance *i* on the mineral surface. On the surface of a given mineral, $\mu_i^0(T,p)$ is equal to the extrapolated value as x_i approaches unity.

2.4. Thermodynamic functions of mineral surface system

A solid–liquid flotation system can be divided into two subsystems: mineral solid surface and aqueous solution. Many mineral types are involved in the flotation process, with each mineral exhibiting unique reagent adsorption characteristics. Therefore, each solid mineral surface is a different subsystem. For simplicity, we consider only the target mineral on which the flotation reagent acts. In this case, the surface of the target mineral and the aqueous solution form two subsystems, with the surface of the mineral considered a subsystem of the flotation process.

In a solid–liquid system in which the flotation of only one type of mineral is considered, the amount of substance increases or decreases as the flotation reagent and other substance components are adsorbed on the mineral surface. Similarly, an increase or decrease is also observed in the aqueous solution. Consequently, the mineral surface becomes an open system relative to the aqueous solution and vice versa. The flotation reagent establishes an equilibrium between the mineral surface system and the aqueous solution system.

The adsorption of a flotation agent on the surface of the mineral will change the Gibbs free energy of the mineral surface in the case of an isothermal or isobaric process with other chemical components unchanged; this property is referred to as the "partial molar Gibbs free energy," that is, the chemical potential of the adsorbed substance, as expressed by μ_i:

$$\mu_i = \left(\frac{\partial G_{\text{sys}}}{\partial n_i}\right)_{T,p,n_C} \tag{38}$$

According to the definition of Gibbs free energy, $G = H - TS$, so $\left(\frac{\partial G}{\partial T}\right)_{p,n_i,n_C} = -S$; consequently $\left(\frac{\partial \mu_i}{\partial T}\right)_{p,n_i,n_C} = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_C}\right]_{p,n_i,n_C} = \left[\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial T}\right)_{p,n_i,n_C}\right]_{T,p,n_C} = \left[\frac{\partial}{\partial n_i}(-S)\right]_{T,p,n_C} = -S_i$; i.e.,

$$S_i = -\left(\frac{\partial \mu_i}{\partial T}\right)_{p,n_i,n_C} \tag{39}$$

According to the thermodynamic theory of chemical reactions, the chemical potential of the adsorption reaction of the flotation agent is given by Eq. (38). According to Eqs. (37)–(39), the partial molar entropy change S_i resulting from the adsorption of flotation agent *i* is given by Eq. (40). The mineral surface entropy resulting from adsorption can be expressed as Eq. (41) when flotation agent *i* is adsorbed on the mineral surface with molar fraction x_i:

$$S_i = -R\ln x_i \tag{40}$$

$$\Delta S = -Rx_i\ln x_i \tag{41}$$

Various flotation agents, if used, will adsorb on the surface of the mineral, with the mineral surface entropy change (ΔS_{surf}) expressed by Eq. (42) when adsorption equilibrium is reached:

$$\Delta S_{\text{surf}} = -R\sum\nolimits_{i=1}^{k} x_i\ln x_i \tag{42}$$

where x_i denotes the molar fraction of the *i*th reagent on the mineral surface.

The x_i values of various agents can be calculated by measuring the adsorption capacities of various flotation agents on the mineral surface, with the entropy change associated with the adsorption of flotation agents on the mineral surface calculated using Eq. (42).

We used numerical simulations to investigate the adsorption of binary, ternary, quaternary, and quintuple flotation reagents on mineral surfaces to gain a deep understanding of how changes in x_i and the number of reagent components affect the ΔS of a mineral surface. The results are shown in Fig. 1, where the horizontal axes represent the mole fraction of the first reagent on the mineral surface, and the vertical axes represent the corresponding entropy change. For a binary reagent system, the mole fraction of the second reagent on the mineral surface is $x_2 = 1 - x_1$, where x_1 is the mole fraction for the first reagent on the mineral surface. However, multiple values of x_i ($i \geq 2$) are possible when three or more reagent components are present and a value for x_1 is given. Therefore, different ΔS values may correspond to the same x_1 in the simulation data. The highest ΔS value is achieved when all x_i values are equal.

2.5. Changes in the thermodynamic function values of a solid–liquid flotation system

The concentration of the flotation reagent added to the aqueous solution is very low; hence, the value of n_i in the aqueous solution system is minuscule before and after reagent adsorption. However, the value of $n_{\text{H}_2\text{O}}$ is enormous; consequently, the entropy change associated with the aqueous solution is almost zero and can be ignored. The entropy change associated with the solid–liquid flotation system after adsorbing the flotation agent on the mineral surface (ΔS_{sys}) is equal to the entropy change for the adsorption of the flotation agent on the mineral surface:

$$\Delta S_{\text{sys}} = -R\sum\nolimits_{i=1}^{k} x_i\ln x_i \tag{43}$$

If the thermal effect δQ for the adsorption of the flotation agent is measured using microthermometry or other methods, and the temperature T of the pulp solution is also measured, then the changes in the thermodynamic energy, enthalpy, and Gibbs free energy of the flotation solid–liquid system (ΔU_{sys}, ΔS_{sys}, and ΔG_{sys}) can be calculated using Eqs. (44)–(46):

$$\Delta U_{\text{sys}} = \delta \text{Q} \tag{44}$$

$$\Delta H_{\text{sys}} = \delta \text{Q} \tag{45}$$

$$\Delta G_{\text{sys}} = \delta \text{Q} + RT\sum\nolimits_{i=1}^{k} x_i\ln x_i \tag{46}$$

According to the second law of thermodynamics, the ad-

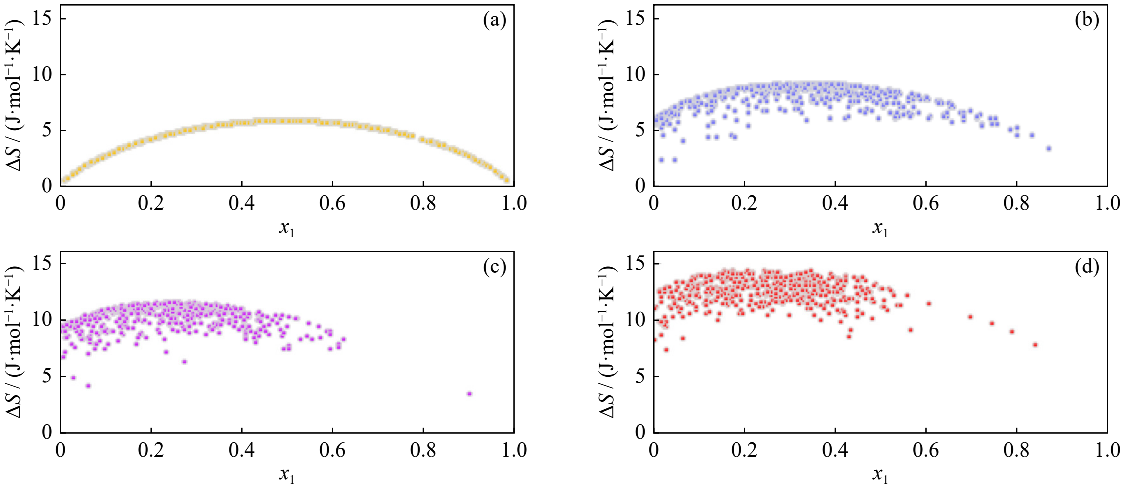

Fig. 1. Simulated entropy changes associated with the adsorption of flotation reagents with different numbers of components on a mineral surface: (a) binary reagents; (b) ternary reagents; (c) quaternary reagents; (d) quintuple reagents.

sorption characteristics of a flotation agent can be determined by measuring changes in the entropy and Gibbs free energy of the mineral surface system associated with the action of the flotation agent, from which flotation agent adsorption on the mineral surface can be regulated. Eq. (43) and Fig. 1 reveal that using multicomponent flotation reagents can increase the entropy change associated with the adsorption of reagents on the mineral surface, thereby improving the flotation effect. Combining reagents that act in synergy improves the physical nature of flotation.

The entropy change of the collector, inhibitor, and activator on the mineral surface associated with adsorption can be expressed by Eqs. (47)–(49), respectively:

$$\Delta S^{\mathrm{c}} = -R\sum\nolimits_{i=1}^{k} x_i^{\mathrm{c}} \ln x_i^{\mathrm{c}} \tag{47}$$

$$\Delta S^{\mathrm{d}} = -R\sum\nolimits_{i=1}^{k} x_i^{\mathrm{d}} \ln x_i^{\mathrm{d}} \tag{48}$$

$$\Delta S^{\mathrm{a}} = -R\sum\nolimits_{i=1}^{k} x_i^{\mathrm{a}} \ln x_i^{\mathrm{a}} \tag{49}$$

where “c” represents the collector, “d” represents the inhibitor, and “a” respresents the activator.

Eqs. (47)–(49) show not only that the combined use of multiple collectors increases the adsorption entropy of the collector on the mineral surface, improves the adsorption efficiency of the collector, and improves the flotation effect but also that the combination of multiple inhibitors or activators can play a synergistic role in improving the change in adsorption entropy of the inhibitor or activator on the mineral surface, thereby improving mineral inhibition or activation; it also reflects the physical nature of inhibitor/activator synergy. Therefore, flotation is referred to as “high-entropy flotation” when a combination of multicomponent flotation agents is used to improve the flotation effect, with Eqs. (47)–(49) providing thermodynamic expressions for high-entropy flotation.

According to Eq. (46), the change in Gibbs free energy associated with the adsorption of the collector, inhibitor, and activator on the mineral surface can be obtained using Eqs. (50)–(52), respectively.

$$\Delta G^{\mathrm{c}} = \delta \mathrm{Q}^{\mathrm{c}} + RT\sum\nolimits_{i=1}^{k} x_i^{\mathrm{c}} \ln x_i^{\mathrm{c}} \tag{50}$$

$$\Delta G^{\mathrm{d}} = \delta \mathrm{Q}^{\mathrm{d}} + RT\sum\nolimits_{i=1}^{k} x_i^{\mathrm{d}} \ln x_i^{\mathrm{d}} \tag{51}$$

$$\Delta G^{\mathrm{a}} = \delta \mathrm{Q}^{\mathrm{a}} + RT\sum\nolimits_{i=1}^{k} x_i^{\mathrm{a}} \ln x_i^{\mathrm{a}} \tag{52}$$

The change in entropy can be used to describe the adsorption behavior of flotation agents on mineral surfaces without measuring the adsorption heat of the flotation agents.

3. Thermodynamic equilibrium of a complex solid–liquid flotation system

In a solid–liquid mineral flotation system, the oxidation and dissolution of minerals, as well as the addition of flotation agents, result in numerous material components in the slurry solution that interact physically and chemically, as well as with the mineral surface, thereby establishing a balance between the material components and phases. These equilibria are controlled by the thermodynamic properties of each material component in the system and the surface properties of the minerals. A thermodynamic state function satisfies certain conditions after equilibrium is reached. Studying the thermodynamic equilibrium of solid–liquid flotation systems can reveal and explain the physical and chemical behavior of the material components and mineral surfaces, thereby providing actual ore flotation guidance.

3.1. Chemical reaction equations for flotation systems

Many chemical reactions occur in an actual solid–liquid flotation system, including the aqueous solution. The chemical reaction for reactants A_1 and A_2 and products A_3 and A_4 can be expressed as follows:

$$\nu_1 \mathrm{A}_1 + \nu_2 \mathrm{A}_2 = \nu_3 \mathrm{A}_3 + \nu_4 \mathrm{A}_4,$$

where ν_i is the coefficient of substance component A_i, which is negative when A_i is a reactant and positive when A_i is a product, and A_i is the number of moles of substance component *i* that changes in a chemical reaction.

Moving the reactants to the left leads to:

$$\nu_3 A_3 + \nu_4 A_4 - \nu_1 A_1 - \nu_2 A_2 = 0.$$

This equation can be expressed in the following way at equilibrium:

$$\sum_i \nu_i A_i = 0 \tag{53}$$

For example, the reaction between zinc carbonate dissolved in smithsonite and sodium sulfide can be expressed as follows:

$$ZnCO_3 + Na_2S = ZnS + Na_2CO_3,$$

which can be represented by the equilibrium reaction Eq. (53) as

$$\sum_i \nu_i A_i = ZnS + Na_2CO_3 - ZnCO_3 - Na_2S = 0.$$

A chemical reaction that occurs between different phases is considered heterogeneous. The adsorption of the components in a mineral slurry solution by the mineral surface is a heterogeneous reaction and can be expressed as

$$\nu_3^\beta A_3^\beta + \nu_4^\alpha A_4^\alpha - \nu_1^\beta A_1^\beta - \nu_2^\alpha A_2^\alpha = 0,$$

or by Eq. (54):

$$\sum_{i,\alpha} \nu_{i\alpha} A_i^\alpha + \sum_{i,\beta} \nu_{i\beta} A_i^\beta = 0 \tag{54}$$

where α represents the liquid phase, and β represents the solid surface term.

For example, the chemical reaction equilibrium equation for the sulfurization of the smithsonite surface becomes:

$$\sum_{i,\alpha} \nu_{i\alpha} A_i^\alpha + \sum_{i,\beta} \nu_{i\beta} A_i^\beta = ZnS^\beta + Na_2CO_3^\alpha - ZnCO_3^\beta - Na_2S^\alpha = 0.$$

A chemical reaction that occurs at the solid–liquid interface during mineral flotation can be considered to involve the transfer of material components between the solid and liquid phases. For example, the sulfurization reaction on the smithsonite surface can be considered to involve the transfer of zinc carbonate to the aqueous solution phase, with the zinc sulfide generated in the aqueous solution phase transferred to the mineral surface. Eq. (55) for phase transfer or phase transition holds when the reaction reaches equilibrium:

$$A_i^\alpha = A_i^\beta \tag{55}$$

3.2. Chemical potential at chemical reaction equilibrium in a solid–liquid flotation system

The Gibbs free energy of a system changes as a chemical reaction proceeds, as described by Eq. (56):

$$dG = -S\,dT + V\,dp + \sum_{i=1}^{k} \mu_i dn_i \tag{56}$$

where $dn_i = \nu_i \varepsilon$, and ε is a small quantity. Thus, Eq. (56) can be expressed as

$$dG_{sys} = -S\,dT + V\,dp + \left(\sum_{i=1}^{k} \nu_i \mu_i\right)\varepsilon \tag{57}$$

The material components in the system reach equilibrium when the chemical reaction reaches equilibrium, and the Gibbs free energy can be expressed as

$$dG_{sys} = -S\,dT + V\,dp \tag{58}$$

The types and quantities of substances in the solid–liquid flotation system that correspond to Eq. (53) do not change when equilibrium is reached; consequently, Eq. (59) holds true based on Eqs. (57)–(58):

$$\sum_{i=1}^{k} \nu_i \mu_i = 0 \tag{59}$$

Eq. (59) describes the equilibrium condition for chemical reactions in aqueous solutions during mineral flotation. In contrast, Eq. (60) holds true for a chemical reaction at the solid–liquid interface, according to Eqs. (55) and (59):

$$\mu_i^\alpha = \mu_i^\beta \tag{60}$$

Eq. (60) indicates that the chemical potentials of a given substance in the aqueous solution and on the mineral surface are equal when the chemical reaction at the solid–liquid interface reaches equilibrium during flotation. The aqueous solution can be regarded as homogeneous phase α in actual mineral flotation, with various mineral surface phases expressed as β, γ…. Flotation systems are complex multiphase systems because of the wide variety of minerals (usually in the tens) present. When material component i reaches equilibrium, its chemical potential must satisfy Eq. (61) according to the balance relationships: $\mu_i^\alpha = \mu_i^\beta$, $\mu_i^\alpha = \mu_i^\gamma$, …,

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \cdots \tag{61}$$

Eq. (61) reveals that adding a certain flotation agent, such as the xanthate–sulfide ore collector, to the solid–liquid flotation system results in the adsorption of the collector components on the various mineral surfaces in the system. The adsorption trend is determined by the chemical potentials of the flotation agent on the various mineral surfaces.

3.3. Partial molar thermodynamic equilibria in the flotation slurry solution

The reagent concentrations change when flotation reagents n_1, n_2, ..., n_k are added in batches to a flotation pulp solution, with partial molar quantities Z_1, Z_2, ..., Z_k, respectively, of the thermodynamic capacity properties of the system also changing. Under isothermal and isobaric conditions, Eq. (27) can be fully differentiated to give Eq. (62):

$$dZ = n_1 dZ_1 + \cdots + n_k dZ_k + Z_1 dnk + \cdots + Z_k dn_k = \sum_{i=1}^{k} n_i dZ_i + \sum_{i=1}^{k} Z_i dn_i \tag{62}$$

with Eq. (63) obtained by comparison with Eq. (25):

$$\sum_{i=1}^{k} n_i dZ_i = 0 \tag{63}$$

Eq. (63) is divided by the total number of moles of the chemical components in the slurry solution to give Eq. (64):

$$\sum_{i=1}^{k} x_i dZ_i = 0 \tag{64}$$

Eqs. (63)–(64) are referred to as Gibbs–Duhem formulas and show that the partial molar amounts of the thermodynamic functions associated with the flotation slurry solution are related in a specific way that manifests as a profit-and-loss relationship. In other words, increasing the partial molar amount of one component decreases the partial molar amounts of the other components.

Eq. (64) becomes Eq. (65) because the partial molar Gibbs free energy is the chemical potential:

$$\sum_{i=1}^{k} x_i \mathrm{d}\mu_i = 0 \tag{65}$$

Eq. (65) is referred to as the "Duhem–Margules formula" and indicates that the chemical potentials of the components in a slurry solution are interrelated. For example, an ammonia component is required to promote the surface sulfurization of copper oxide minerals when ammonium sulfate or ammonium carbonate is added to a copper oxide ore flotation slurry solution. The same results should be obtained when the same number of moles of ammonia are added. However, these two ammonium salts exert different effects, possibly because of the different chemical potentials of the sulfate and carbonate components that change the differentiation potentials of the other components in the system, as well as differences in the chemical potentials of the ammonia components, resulting in different sulfurization effectiveness.

3.4. Thermodynamic equilibrium equations for complex solid–liquid flotation systems

High-entropy flotation is a method for improving mineral flotation efficiency by increasing the number of flotation reagent components, using them in combination, and exploiting reagent synergy to increase the adsorption entropy of the flotation reagents and reduce the Gibbs free energy of the solid–liquid flotation system. From Eq. (43) ($\Delta S_{\mathrm{sys}} = -R\sum_{i=1}^{k} x_i \ln x_i$), we infer that the entropy changes more during the adsorption process when more types of mineral flotation reagents are adsorbed. A greater variety of collectors leads to a larger entropy change during collector adsorption on the mineral surface when the flotation reagents are collectors, resulting in more stable adsorption. Similarly, more activator types lead to a larger entropy change during activator adsorption on the mineral surface, resulting in more stable adsorption, while a greater variety of inhibitors leads to a larger entropy change for inhibitor adsorption on the mineral surface, leading to more stable adsorption.

Eq. (43) provides a maximum value when the molar fractions x_i of the various flotation reagents adsorbed on the mineral surface are equal, leading to

$$\Delta S_{\max} = -R\ln k \tag{66}$$

Flotation reagent adsorption on the mineral surface cannot be artificially controlled on the basis of dosage in a mineral flotation system; such adsorption is controlled by the chemical potentials of the reagents on the mineral surface and in the aqueous solution (i.e., it must satisfy the condition $\mu_i^{\alpha} = \mu_i^{\beta}$, as shown in Eq. (60)). The chemical potential of flotation reagent i in the aqueous solution is equal to that on the mineral surface when adsorption equilibrium is reached.

Various types of mineral and flotation reagents are adsorbed to different extents on surfaces in an actual mineral flotation process. The condition $\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma} = \cdots$, which represents chemical equilibrium (as shown in Eq. (61)), is satisfied after reaching adsorption equilibrium. μ_i^{α} of flotation reagent i in the pulp solution can be controlled by adjusting the quantity of the reagent in the pulp solution. However, when added to the pulp solution, flotation reagent i chemically reacts with certain components in the solution. The concentration of reagent i in the solution is only represented as x_i^{α} when these reactions reach equilibrium (i.e., Eq. (59); $\sum_{i=1}^{k} \nu_i \mu_i = 0$). At this point, the chemical potential of flotation reagent i in the pulp solution is determined by $\mu_i^{\alpha} = \mu_i^{\alpha 0}(T, p) + RT\ln x_i^{\alpha}$. However, the standard chemical potential $\mu_i^{\alpha 0}(T, p)$ of the flotation reagent depends on not only the pure flotation reagent but also the properties of the mineral surfaces; this information is currently difficult to obtain, which complicates using Eq. (61) to calculate the μ_i^{β} of flotation reagent i adsorbed on the target mineral surface. Therefore, the amount of flotation reagent adsorbed on the mineral surface in the pulp solution can only be obtained using actual measurements.

Chemical reactions that occur between the various reagent components must be considered when multicomponent flotation reagents are used in an actual flotation process. If some of the added flotation reagents chemically react in a manner detrimental to flotation, they must be added in separate batches to avoid undesirable interactions. Once a flotation reagent is adsorbed onto a mineral surface, the addition of another flotation reagent disrupts the original adsorption equilibrium, and a new equilibrium is established on the basis of the balance condition expressed in Eq. (65) (i.e., $\sum_{i=1}^{k} x_i \mathrm{d}\mu_i = 0$). This new equilibrium may result in the previously adsorbed reagent undergoing partial desorption or further adsorption, as indicated by Eq. (65).

Flotation reagent adsorption on a mineral surface is controlled by Eqs. (60), (61), and (65); hence, accurately controlling the adsorption of a specific flotation reagent on a mineral surface by simply adjusting the concentration of the reagent in the pulp solution is difficult. When multiple component flotation reagents reach adsorption equilibrium, the maximum change in the adsorption entropy of these reagents is not given by Eq. (66) but rather by the maximum value under the dosage conditions of the selected flotation reagents. Achieving an equal molar fraction of adsorbed flotation reagents on mineral surfaces is unnecessary and difficult. The adsorption process must simultaneously satisfy the thermodynamic equilibrium relationships represented by Eq. (67):

$$\mu_i = \mu_i^{0}(T, p) + RT\ln x_i \tag{67a}$$

$$\mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\gamma} = \cdots \tag{67b}$$

$$\sum_{i=1}^{k} \nu_i \mu_i = 0 \tag{67c}$$

$$\sum_{i=1}^{k} x_i \mathrm{d}\mu_i = 0 \tag{67d}$$

On the basis of this theoretical analysis provided, we conclude that high-entropy flotation using multicomponent flotation reagents increases the entropy change during flotation reagent adsorption on mineral surfaces, enhances the stability of the adsorbed reagent, and improves mineral flotation performance according to the entropy increase rule associated with the second law of thermodynamics. However, because of the complexity of a flotation system, flotation reagent adsorption is controlled by the thermodynamic equilibrium relationships represented by Eq. (67) in practical applications. Unfortunately, pure theoretical calculations are not feasible, a combination of theory and experiments is necessary, and experimental data on flotation reagent adsorption on mineral surfaces must be obtained, followed by determining thermodynamic functions, such as changes in the entropy and Gibbs free energy associated with the adsorption process. These data can provide guidelines for the development of practical mineral flotation processes.

3.5. Effect of mineral surface homogenization and its regulation

Flotation is a process that uses flotation reagents to modify the physical and chemical properties of mineral surfaces to separate and concentrate minerals using bubbles as the medium. Processes such as mineral surface oxidation, dissolution, and the release of ore–fluid components from fluid inclusions within minerals during comminution and the flotation water source can affect the composition of the pulp before adding any flotation reagent. The equilibrium represented by Eq. (67a) ($\mu_i^\alpha = \mu_i^{\alpha 0}(T,p) + RT\ln x_i^\alpha$) and Eq. (67b) ($\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \cdots$) will be reestablished following a slight change in the quantity of a certain substance i in the mineral pulp (i.e., a variation in x_i^α in Eq. (67a)). This process is known as the "surface homogenization effect" in minerals, and its physical meaning can be expressed as follows: The dissolution of component i from the surface of a mineral in the mineral pulp increases the molar fraction x_i^α of component i in the pulp and subsequently changes the chemical potential μ_i^α of component i in the pulp. According to the equilibrium relationship given by Eq. (67b), the chemical potentials of component i on the surfaces of other minerals also change. The original equilibrium is disrupted and a new equilibrium is established on the basis of the thermodynamic equilibrium equations. Consequently, component i on the surface of one mineral is transferred to other mineral surfaces. Generally, the surface components of all minerals tend to dissolve to varying degrees in the mineral pulp, ultimately leading to various minerals with similar surface components and properties according to the thermodynamic equilibrium relationships described by Eq. (67).

The addition of flotation reagent component i also alters the chemical potential of component i in the mineral pulp; component i is adsorbed onto the surfaces of various minerals according to the equilibrium relationship described by Eq. (67b). The amount of flotation reagent component i adsorbed depends on the standardized chemical potentials of this component on the surfaces of the various minerals. Greater differences in the surface properties of these minerals lead to greater differences in the standardized chemical potentials of component i adsorbed on the mineral surfaces. In addition, the adsorption of flotation reagent component i onto various mineral surfaces leads to mineral surface homogenization.

Mineral surface homogenization commonly occurs in complex solid–liquid flotation systems. For example, the copper, lead, and zinc components dissolve from their respective mineral surfaces into the aqueous solution and subsequently adsorb onto the surfaces of other minerals in copper–lead–zinc sulfide ore flotation systems, thereby reaching chemical equilibrium, as described by Eq. (61). The copper mineral surface contains lead and zinc components in this equilibrium state; the lead mineral surface, copper and zinc components; and the zinc mineral surface, copper and lead components. This homogenization effect is an inevitable result of the chemical equilibrium conditions described by Eq. (61). The quantities of various components on mineral surfaces are determined using Eq. (61). Similarly, the dissolution and dissociation of mineral surface components result in fluoride, carbonate, and tungstate ions in the mineral pulp solution in fluorite, calcite, and scheelite flotation systems; these ions are adsorbed onto different mineral surfaces according to Eq. (61), leading to carbonate and tungstate ions on the fluorite surface, fluoride and carbonate ions on the scheelite surface, and fluoride and tungstate ions on the calcite surface. This process contributes to the mineral surface homogenization trend.

Flotation is used to separate and enrich minerals; in general, surface homogenization, which is determined by thermodynamic equilibrium conditions, is unfavorable for separating minerals by flotation. Therefore, flotation reagents are selected, and various mineral surface properties are controlled to minimize mineral surface homogenization during flotation.

According to its physical nature, the surface homogenization effect is pronounced for ore flotation systems in which minerals have strong surface solubilities, which results in poor flotation selectivities. Adding chemical agents can control mineral surface dissolution and eliminate inevitable ions in solution before adding flotation reagents, such as collectors, activators, and depressants, which helps reduce surface homogenization involving target and gangue minerals, thereby facilitating subsequent flotation separation.

4. High-entropy flotation

4.1. Adsorption equilibrium constants and flotation reagent selection

High-entropy flotation involves using multicomponent reagents; consequently, the selection of appropriate flotation reagents is a prerequisite for high-entropy flotation. According to previous theoretical analyses, different types, amounts, and addition sequences of flotation reagents result in different adsorption entropies on the mineral surface. However, a larger change in adsorption entropy indicates that the multicomponent flotation reagent is more stable under the selected reagent conditions, although this attribute is insufficient for good mineral flotation performance. Flotation reagent type, dosage, and sequence must be studied to achieve good flotation results.

(1) Selecting the flotation reagent.

Flotation agents are mainly selected on the basis of production practice experience and previous research results in flotation experiments involving actual ores, with solubility product theory, double-layer theory, and adsorption theory mainly relied on for guidance. Solubility product theory is most commonly used; it states that the adsorption capacity of a flotation agent on a mineral surface correlates positively with its solubility product constant in aqueous solution; in other words, flotation agents and metal ions with lower solubility product constants exhibit stronger flotation agent/mineral surface adsorption capacities.

Flotation reagent A with ion A^- forms precipitate MeA when it reacts with metal-ion Me^+ in aqueous solution, with solubility product constant K_{sp} given by Eq. (68) at reaction equilibrium:

$$K_{sp} = [Me^+][A^-] \tag{68}$$

The Gibbs free energy change for this chemical reaction is given by:

$$\Delta G = RT \ln K_{sp} \tag{69}$$

Commonly used flotation reagents that react with metal ions generally have negligible K_{sp} values but enormous and negative ΔG values for the reaction, which indicates that the flotation reagents react to completion with these metal ions at very high rates. However, the amounts of reagent adsorbed on mineral surfaces in actual flotation systems are far from those expected on the basis of solubility product theory. Indeed, the amount of reagent adsorbed on the mineral surface is limited, and its adsorption rate is relatively low because the adsorption of flotation reagents on mineral surfaces does not obey Eqs. (68)–(69); rather, they are controlled by the thermodynamic equilibrium relationships shown in Eq. (67). However, in the absence of specific data suitable for Eq. (67), flotation agents can be selected on the basis of Eq. (68), industrial production experience, and previous research results. Using four-component flotation reagents numbered according to their effectiveness as examples, the best-performing flotation reagent was determined to be 1, followed by 2, and so on, resulting in flotation reagents ordered as follows: 1, 2, 3, and 4. In the flotation practice of low-grade refractory oxidized copper ore, a multicomponent collector is usually formed by mixing collectors such as amyl xanthate, butyl xanthate, ammonium dibutyl dithiophosphate, and hydroxamic acid to enhance the recovery of oxidized copper ore. Among these collectors, amyl xanthate has the best collection performance and is determined as collector 1. Butyl xanthate, ammonium dibutyl dithiophosphate, and hydroxamic acid are determined as collectors 2, 3, and 4, respectively.

(2) Adsorption equilibrium constants for flotation reagents on mineral surfaces.

As discussed above, using solubility product theory to determine the adsorption capacity of flotation reagents on mineral surfaces can lead to considerable errors, inaccuracies, and sometimes contradictory results, which are mainly ascribable to the components on the mineral surface constrained by the mineral surface, with a very large difference in chemical potentials between the free components in solution and the components that can react with the flotation reagents in the solution. The reactivities of the free components on the mineral surface are very low to the extent that they should not chemically react according to solubility product theory. Therefore, providing practical guidance for actual mineral flotation systems by studying the adsorption equilibrium constants of flotation reagents on mineral surfaces is important.

According to Eq. (67a), the chemical potential of a flotation reagent in a slurry solution is given by $\mu_i^\alpha = \mu_i^{\alpha 0}(T,p) + RT\ln x_i^\alpha$. Similarly, the chemical potential of a flotation reagent on a mineral surface is $\mu_i^\beta = \mu_i^{\beta 0}(T,p) + RT\ln x_i^\beta$. Formula (70) is valid according to the phase equilibrium condition of Eq. (67b) ($\mu_i^\alpha = \mu_i^\beta$):

$$\mu_i^{\alpha 0}(T,p) + RT\ln x_i^\alpha = \mu_i^{\beta 0}(T,p) + RT\ln x_i^\beta \tag{70}$$

Eq. (71) is obtained by rearranging the terms in Eq. (70):

$$\frac{x_i^\beta}{x_i^\alpha} = \exp\left(\frac{\mu_i^{\alpha 0}(T,p) - \mu_i^{\beta 0}(T,p)}{RT}\right) \tag{71}$$

where x_i^β is the mole fraction of flotation reagent i adsorbed on the mineral surface, which is equivalent to the amount adsorbed. x_i^α is the mole fraction of flotation reagent i in the slurry solution at adsorption equilibrium, which is equivalent to the residual reagent concentration in the slurry solution. $\mu_i^{\alpha 0}(T,p) - \mu_i^{\beta 0}(T,p)$ is the difference between the standard chemical potentials of the flotation reagent in the slurry solution and on the mineral surface or the difference between the standard partial molar Gibbs free energies; it represents the adsorption ability of flotation reagent i on the mineral surface, which depends on the properties of flotation reagent i and the mineral surface.

In practical mineral flotation, the standard chemical potential that reflects the properties of a flotation reagent can be obtained from relevant chemical manuals. However, the standard chemical potentials associated with mineral surface properties and the standard chemical potentials of flotation reagents when adsorbed on mineral surfaces under saturation conditions are not yet available, and theoretically calculating the adsorption capacities of flotation reagents on mineral surfaces using Eq. (71) cannot be fully achieved. However, the amounts of flotation reagent adsorbed on mineral surfaces can now be accurately determined, allowing for theoretical data on the adsorption capacity of a certain flotation reagent on a certain mineral surface to be obtained from adsorption measurements.

The amounts of flotation reagent adsorbed on mineral surfaces can be determined in various ways. ICP-MS provides relatively accurate data for metal ions, while ultraviolet spectrophotometry is used to determine the concentrations of organic flotation agents in aqueous solutions, and liquid chromatography and other methods obtain the concentrations of flotation agent components. Consequently, the residual concentration method can be used to determine the amount of flotation reagent adsorbed on a mineral surface.

Generally, mineral surfaces adsorb different amounts depending on the concentrations of flotation reagents in a pulp solution. A higher concentration of flotation reagent added to the pulp solution results in a greater amount adsorbed on the mineral surface; conversely, a lower concentration in the pulp solution leads to a lower amount adsorbed on the mineral surface. The adsorption equilibrium constant of the mineral surface for a flotation reagent (K_{ad}), defined as the ratio of the number of moles of flotation reagent adsorbed onto the mineral surface to the number of moles of residual flotation reagent in the solution at a given pulp concentration, is given as

$$K_{ad} = \frac{\Gamma_{xi}/\Gamma^{c}_{xi}}{x_i^{\alpha}} = \frac{kx_i^{\beta}}{x_i^{\alpha}} = k\exp\left(\frac{\mu_i^{\alpha0}(T,p)-\mu_i^{\beta0}(T,p)}{RT}\right) \quad (72)$$

where k is a scale factor, which, for a single mineral, is the adsorption amount measured by gradually increasing the flotation reagent concentration in the slurry solution. The amount of flotation reagent is small, and the adsorption capacity of the mineral surface is very low at a fixed temperature. Eq. (72) reveals that $\frac{\mu_i^{\alpha0}(T,p)-\mu_i^{\beta0}(T,p)}{RT}$ is a constant; i.e., K_{ad} is a determined constant. The adsorption equilibrium constant changes with the concentration of the flotation reagent in solution when the amount adsorbed is large; that is, the amount adsorbed and the flotation reagent concentration are no longer linearly related, which is ascribable to changes in the properties of the mineral surface as flotation reagents are adsorbed; hence, they are no longer self-properties of the mineral surface, and the standard chemical potential $\mu_i^{\beta0}(T,p)$ is no longer a constant of the flotation reagent. The same flotation reagent has various saturated adsorption equilibrium constants that are mineral surface-dependent. A larger K_{ad} value corresponds to stronger flotation reagent adsorbability on the mineral surface. Because the adsorption equilibrium constant is a comprehensive manifestation of various flotation theories, such as solubility product theory, double-layer theory, and adsorption theory, it originates from the thermodynamic equilibrium equations of the solid–liquid system and is fundamental for mineral flotation thermodynamics. The adsorption capacities and selectivities of flotation reagents on different mineral surfaces can be determined using the saturated adsorption equilibrium constant.

Using the above method, saturation adsorption equilibrium constants of flotation reagents on a mineral surface can be obtained, and then, using these equilibrium constants, the adsorption capacities and selectivities of these flotation agents on this mineral surface can be determined. Therefore, the equilibrium constants for the saturated adsorption of flotation reagents on mineral surfaces can be used as an important basis for selecting flotation reagents. Several inhibitors of chalcopyrite used in copper–molybdenum separation, several inhibitors of galena in copper–lead separation, several collectors used in zinc sulfide flotation systems, several metal-ion activators in scheelite flotation, and several commonly used collectors in tin flotation were examined as examples. The adsorption equilibrium constant of each flotation agent on the surface of the corresponding mineral was determined and is shown in Table 1 and Figs. 2–6.

Table 1. Adsorption equilibrium constants of several minerals for flotation reagents

Minerals	Flotation reagents	K_{ad} / 10^5
Chalcopyrite	Sodium sulfide (Na_2S)	7.27
	Sodium thioglycolate (STG)	3.55
	L-cysteine (L-cys)	2.35
	Sodium dithiocarbonate (NaDTC)	6.35
Galena	Pyrogallic acid (PA)	1.12
	Polymaleic acid (PMA)	0.819
	Sodium silicate (Na_2SiO_3)	0.194
	Sodium thiophosphate (Na_3SPO_3)	0.13
Smithsonite	Dodecylamine (DDA)	6.94
	Isoamyl potassium xanthate (KAX)	2.79
	Octyl hydroxamic acid (OHA)	3.34
	Sodium diethyl dithiocarbamate (DDTC)	4.00
Scheelite	Mn^{2+} ($Mn(NO_3)_2$)	31.1
	Hg^{2+} ($Hg(NO_3)_2$)	0.194
	Pb^{2+} ($Pb(NO_3)_2$)	16.3
	Benzohydroxamic acid (BHA)	0.18
Cassiterite	Styrene phosphonic acid (SPA)	2.15
	Salicylhydroxamic acid (SHA)	2.61
	Octyl hydroxamic acid (OHA)	7.54
	Isopropanolamine dodecylbenzenesulfonat (DBIA)	12.6

The solubility product constants of flotation agents and substances in aqueous solutions also need to be determined experimentally but have considerable errors and are unreliable. Therefore, selecting the flotation reagents for practical mineral flotation according to the experimentally determined saturation adsorption equilibrium constants of flotation reagents on mineral surfaces is highly reliable and feasible.

(3) Determining changes in adsorption entropy and Gibbs free energy for multicomponent flotation reagents on mineral surfaces.

Eqs. (47)–(49) show that the change in adsorption entropy associated with multicomponent flotation reagents on a mineral surface can be calculated by measuring the mole fraction of the adsorbed flotation reagent on the mineral surface, which, in turn, is obtained by determining the amount adsorbed. The adsorption capacity of each flotation reagent is measured individually or simultaneously in the absence of considerable interactions among the flotation reagent components. The amounts of various flotation agents adsorbed are determined individually. Initially, the flotation agent with the best flotation effect is selected and allowed to react with the mineral surface at a predetermined concentration. The residual concentration in the slurry solution is measured when adsorption equilibrium is reached, and the amount of flotation agent adsorbed on the mineral surface is determined. The second flotation reagent is then added and its residual concentration in the solution is measured to determine its amount adsorbed. Hence, the amounts of multicomponent flotation reagents adsorbed on the mineral surface are obtained. However, the thermodynamic equilibrium relationships

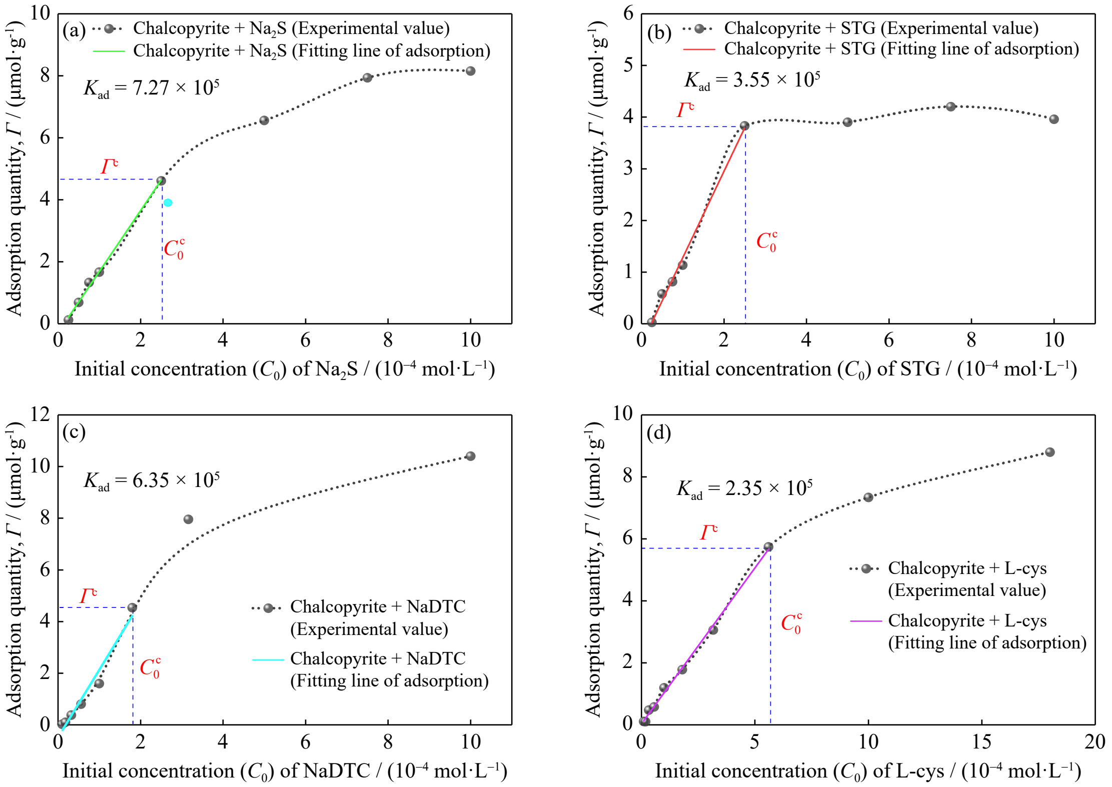

Fig. 2. Adsorption equilibrium constants for several chalcopyrite inhibitors.

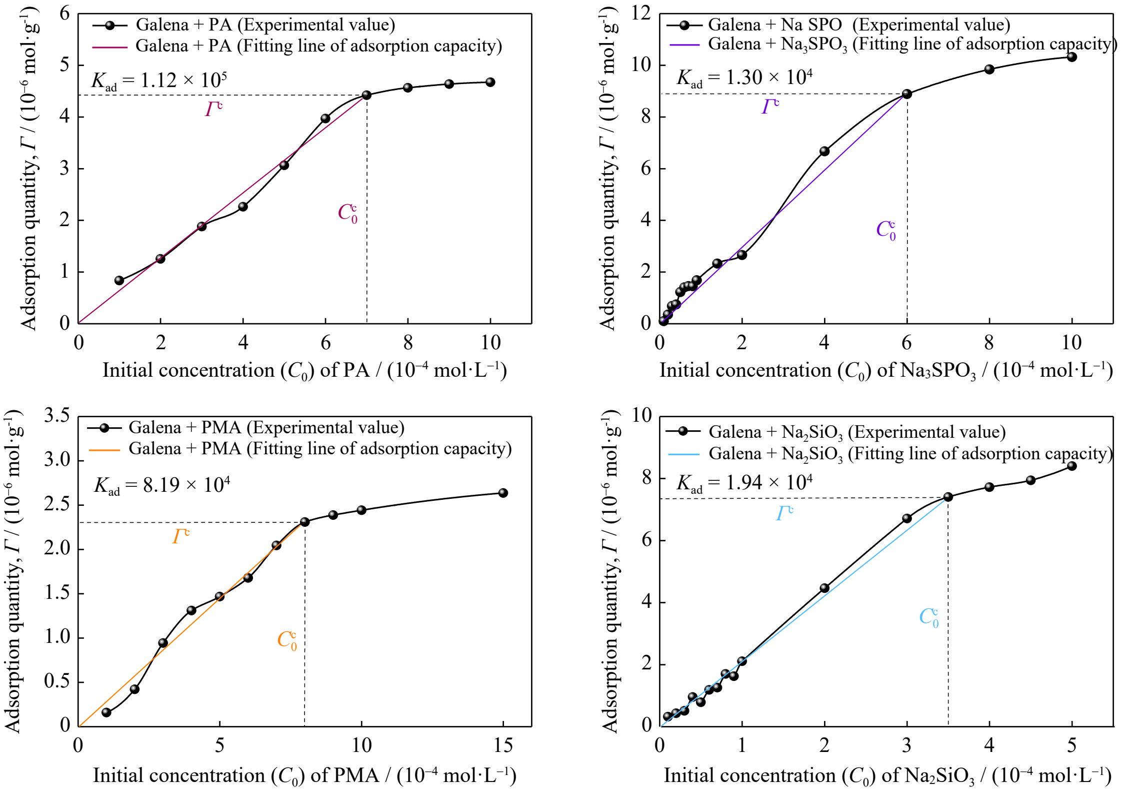

Fig. 3. Adsorption equilibrium constants for several galena inhibitors.

shown in Eq. (67) must be used to break the original equilibrium and establish a new equilibrium on the mineral surface and in the slurry solution whenever a new flotation reagent is added during the adsorption measurement process, which leads to the desorption of the flotation reagent originally adsorbed on the mineral surface, as well as further adsorption. Accurate measurements must consider this variation, and the amount of the previous flotation reagent or reagents adsorbed must be sequentially corrected to obtain the correct amount adsorbed on the mineral surface. Simultaneous determination is another method for obtaining the amounts of multicomponent flotation reagents adsorbed, which involves

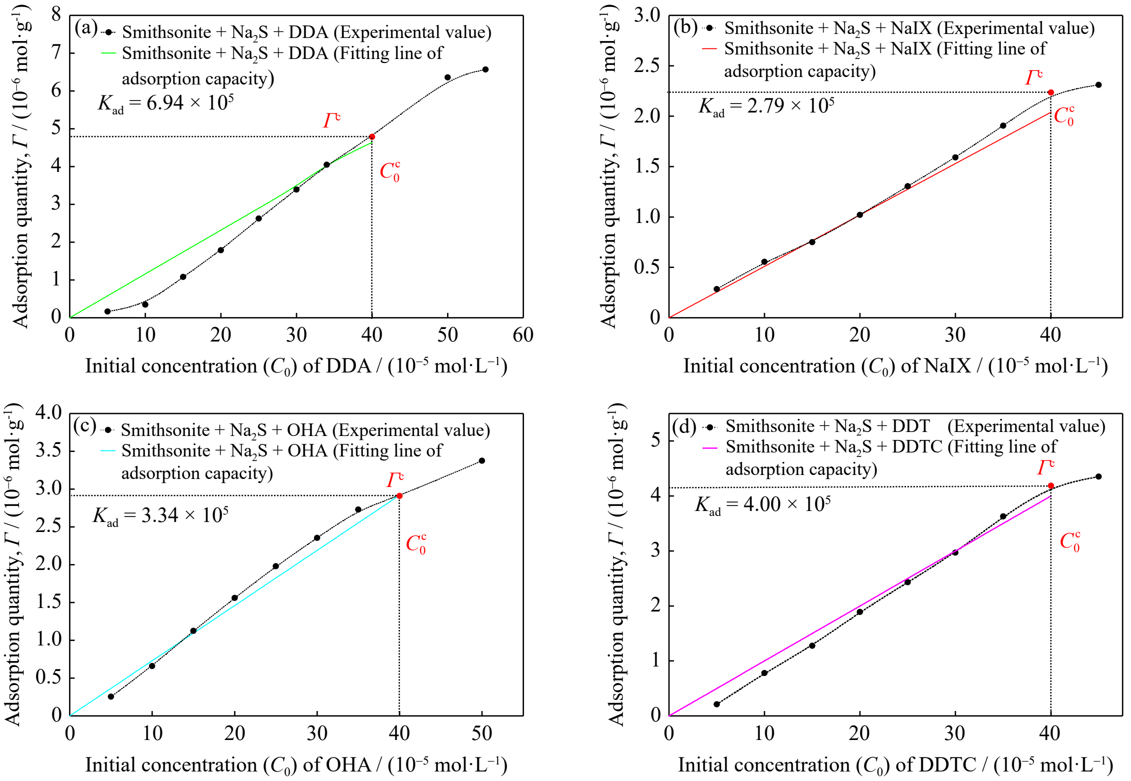

Fig. 4. Adsorption equilibrium constants for several smithsonite flotation collectors.

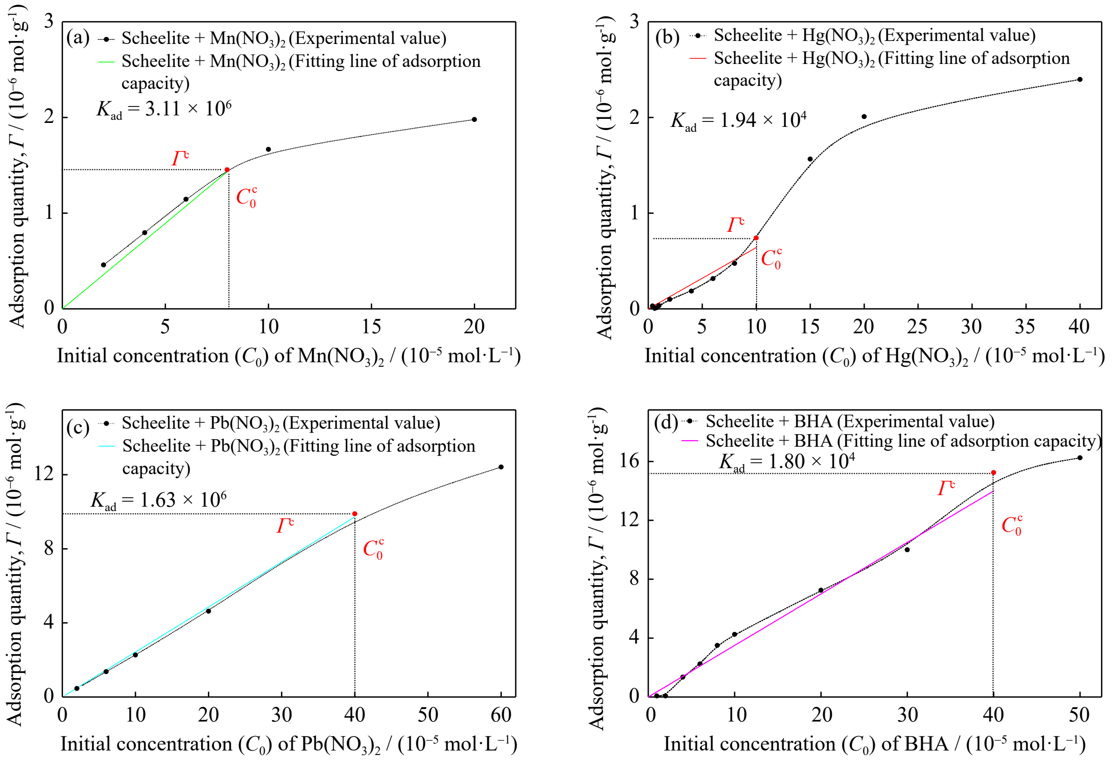

Fig. 5. Adsorption equilibrium constants of the Mn^{2+}, Hg^{2+}, and Pb^{2+} activators and the benzohydroxamic acid collector in the scheelite flotation system.

adding all flotation reagents to the slurry solution and measuring the residual concentration of each flotation reagent in the slurry solution after reaching equilibrium, from which the amount of each flotation reagent adsorbed onto the mineral surface can be calculated. This method yields an adsorption amount near the actual situation because the solid–liquid flotation system (Eq. (67)) is fully equilibrated at this time. However, this method is limited in its ability to detect the residual concentration of each flotation reagent in the pulp solution. For example, accurately determining the residual concentrations of multicomponent collectors whose ultraviolet absorption peaks overlap is difficult.

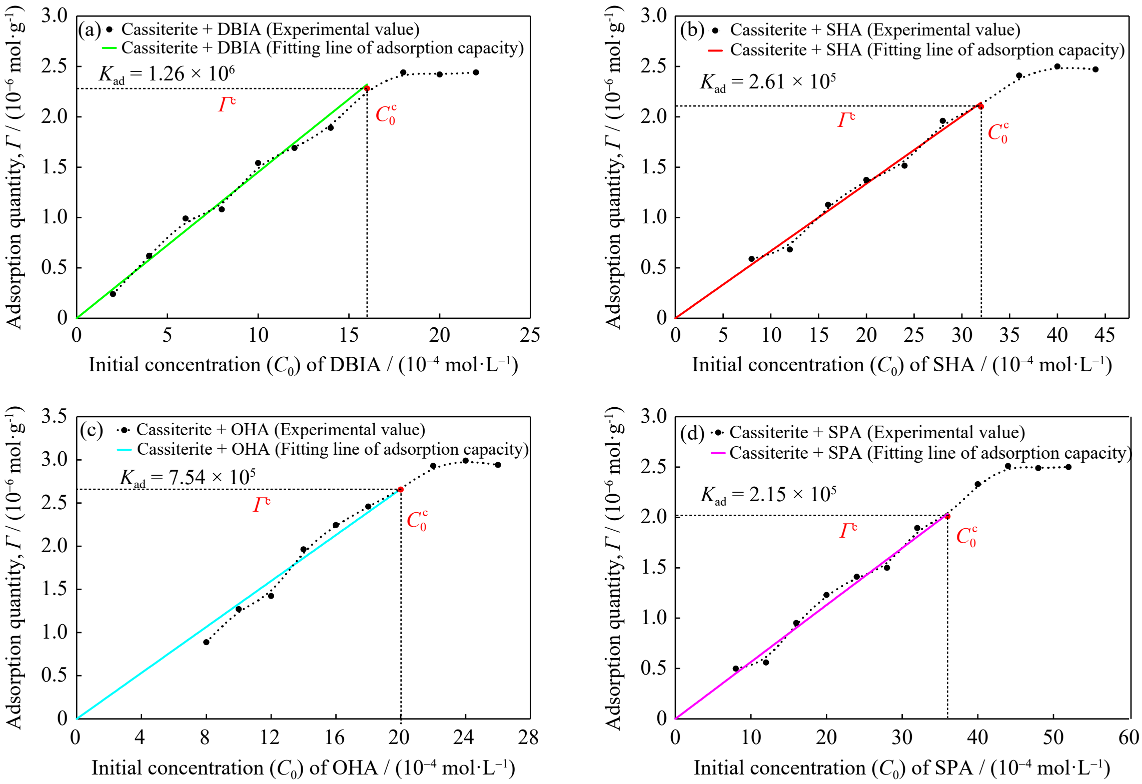

Fig. 6. Adsorption equilibrium constants of several cassiterite flotation collectors.

The mole fraction of each flotation agent adsorbed on the mineral surface is calculated after measuring the amount of each multicomponent flotation agent adsorbed. In the case of a four-component collector flotation system, the mole fraction of an adsorbed collector is the adsorption amount of this collector on the mineral surface divided by the sum of the adsorption amounts of all four collectors. The adsorption effect is not represented by the change in the adsorption entropy during the adsorption of a single-component collector but rather by the saturated adsorption equilibrium constant, which characterizes the adsorption performance of the collector. The change in the adsorption entropy of a collector on the mineral surface is calculated according to Eq. (47) using the adsorption mole fraction of the multicomponent collector for a multicomponent collector. The change in the Gibbs free energy during multicomponent collector adsorption is calculated using Eq. (50) when microcalorimetry is used to determine the thermal effects of various collector adsorption processes.

Similarly, changes in the adsorption and activation entropies associated with multicomponent inhibitors and multicomponent activators on mineral surfaces can be calculated by measuring the amounts of inhibitor and activator absorbed on the mineral surfaces and then applying Eqs. (48)–(49). In addition, microcalorimetry and Eqs. (51)–(52) can be used to determine changes in the Gibbs free energy of inhibition and activation during the adsorption of multicomponent inhibitors and multicomponent activators.

Some flotation agents regulate mineral flotation not by adsorbing their components on the mineral surface but by producing new species through reactions involving the mineral surface or changing the type of original species or its quantity on the mineral surface. If the differences in the numbers and types of species on the mineral surface before and after the addition of the flotation reagents are determined, the abovementioned entropy change formula can be used to calculate entropy and Gibbs free energy changes for surface chemical reactions involving such flotation reagents, after which the effect of the flotation reagent can be determined.

4.2. High-entropy flotation methods for actual ore

A simple flotation reagent system can achieve good flotation results according to production practice experience and previous experimental research results for practical ores with simple mineral compositions and good target mineral floatabilities. However, simple reagent systems often fail to achieve satisfactory flotation results for complex ores with complex mineral compositions, poor target mineral floatabilities, and target/gangue mineral separation difficulties. The development and use of simple ores cannot meet the demands of the continuing industrialization of human society, and required minerals are mostly associated with low-grade and difficult-to-handle complex ores. Multicomponent flotation agents are inevitably used to process such difficult and complex ores. The adsorption of multicomponent flotation agents in a solid–liquid complex flotation system follows the thermodynamic equilibrium relationships in Eq. (67) when ores are treated with multicomponent collectors, multicomponent depressants, and multicomponent activators.

(1) High-entropy flotation.

Multiple component collectors can be used to synergistically improve the floatabilities of minerals and achieve efficient flotation recoveries for oxidized ores, such as zinc oxide, copper oxide, stannite, and titanium–iron ore, which have relatively poor floatability. The recovery purpose and the types and contents of recoverable and gangue minerals should be determined through mineralogical research for such ores. The type of multicomponent collector should be selected according to the mineral recovery purpose.

The collector type is selected on the basis of the saturation adsorption equilibrium constants of various collectors on mineral surfaces, production practice experience, and previous experimental research results. The collectors are numbered according to their collection performance, with the collector with the best collecting performance numbered 1, that with the second-best performance numbered 2, and so on, to afford collector numbers 1, 2, 3, and 4. The collector with the best performance in collector dosage experiments is selected as the main collector, while the others are auxiliary collectors. The collector with the second-best performance under the optimal dosage conditions of the main collector is selected as the second component collector, and its dosage is optimized. The dosages of the third and fourth component collectors are similarly determined after determining the optimal dosage of the second component collector, leading to the multicomponent collector system.

The dosage range is selected near the determined dosage to perform multifactor orthogonal experiments using the multicomponent collector based on the data acquired through single-factor experiments involving each component collector. The high-entropy multicomponent collector-based flotation method is then confirmed through verification experiments.

Taking the flotation of low-grade refractory oxidized lead zinc ore in Lanping as an example, we adopted a separation process of lead first and then zinc. We tested the effect of increasing the number of collector components in a multicomponent collector system (DDA, KAX, ADD, and OHA) on zinc flotation indexes. The flotation flowchart is shown in Fig. 7, and the results are shown in Table 2. According to the analysis of the data results in Table 2, the zinc recovery in zinc roughing operation is only 74.08% when only DDA is used as the collector. By applying the high-entropy flotation theory under the DDA–KAX–ADD–OHA quaternary collector system, the zinc recovery in zinc roughing operation was considerably improved to 86.09%. The flotation test results further validate the high-entropy flotation theory.

The abovementioned procedure is the best method because the solid–liquid flotation system adheres to the thermodynamic equilibrium conditions expressed by Eq. (67). This method, when used with Eq. (47) to calculate the entropy change associated with monomineral adsorption by a multicomponent collector to determine surface adsorption amounts, will yield entropy changes that are greater than that of a single- or binary-component collector.

The best-performing collector for an actual flotation process may be expensive and include hydroxyacid-chelating collectors or arsenic acid types, which are toxic and restricted for industrial use. In these cases, high-entropy flotation can considerably reduce the dosages of these collectors, while other collector components can be used to increase changes in entropy on mineral surfaces to compensate for the negative impact of lower dosages of the main collectors.

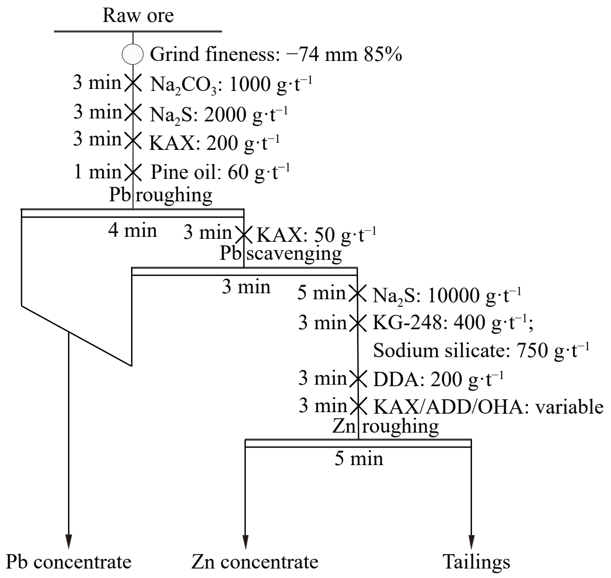

Fig. 7. Flowchart of the open-circuit flotation process on Lanping zinc oxide ores.

Table 2. Flotation test results of different collector systems

Collector component	Product	Yield / %	Zn grade / %	Zn recovery / %
200 g·t^{-1} DDA	Pb Concentrate	7.90	5.11	5.85
	Zn Concentrate	20.39	25.06	74.08
	Tailing	71.72	1.93	20.07
	Feed	100.00	6.90	100.00
200 g·t^{-1} DDA; 400 g·t^{-1} KAX	Pb Concentrate	7.29	5.31	5.67
	Zn Concentrate	22.39	24.84	81.45
	Tailing	70.33	1.25	12.88
	Feed	100.00	6.83	100.00
200 g·t^{-1} DDA; 400 g·t^{-1} KAX; 200 g·t^{-1} ADD; 100 g·t^{-1} OHA	Pb Concentrate	8.02	5.02	5.71
	Zn Concentrate	30.37	20.00	86.09
	Tailing	61.61	0.94	8.21
	Feed	100.00	7.06	100.00

(2) High-entropy depression flotation.

Separating and recovering minerals with similar floatabilities, such as copper–molybdenum, copper–lead, copper–zinc, tungsten–tin, and calcium-containing minerals, is often necessary when flotation processing complex ores. Separating minerals with similar floatabilities has always been difficult in the mineral processing field. High-entropy depression flotation considerably improves the separation of such minerals. According to Eq. (48), the entropy change associated with inhibition using a multicomponent depressant, in theory, considerably increases the entropy change associated with the adsorption of the depressant on the mineral surface, thereby promoting depressant adsorption stability on the mineral surface, which improves the depressant effect.

The saturation adsorption equilibrium constants for depressants on the surfaces of minerals that must be separated by flotation can be determined from previous experimental research results and production practice experience and used to select the depressant type. The depressive performance of depressants is verified through flotation experiments to determine the main and auxiliary depressants. Sequential experiments are conducted to determine multicomponent depressant systems under the optimal dosage conditions of the main depressants. Dosage ranges are selected for multifactor orthogonal experiments based on the determined multicomponent depressant dosages to determine the optimal multicomponent depressant dosages. Verification experiments are conducted to confirm the final multicomponent depressant systems.

The main depressants are sometimes toxic substances, such as cyanide or permanganate salts, and are restricted for industrial use in a similar manner to how collectors are selected. In these cases, dosages can be considerably reduced by replacing them with multicomponent depressants. Although auxiliary depressants may not perform as well as the main depressant, the use of multicomponent depressants considerably increases the entropy change for depressant adsorption on mineral surfaces and improves depression effectiveness by increasing adsorption stability.

Taking the copper–molybdenum bulk concentrate from a mine in Yunnan as a case study and referring to the experimental flowchart in Fig. 8, we compared the flotation test indices obtained from single-use Na_2S conditions and high-entropy depression conditions composed of Na_2S, L-cys, STG, and NaDTC through one roughing flotation. The experimental results are presented in Table 3, where Ind. and Cum. denote individual and cumulative, respectively. When using 6000 g/t Na_2S alone, the yield of Mo concentrate was 10.54%, the Mo grade in the Mo concentrate was 5.94%, and the Mo recovery was 84.33%. When using a quaternary depressant composed of 1500 g/t Na_2S, 260 g/t L-cys, 180 g/t STG, and 300 g/t NaDTC under identical remaining test conditions, the yield of Mo concentrate decreased to 8.98%, the Mo grade in the Mo concentrate increased to 7.22%, and the Mo recovery increased to 87.69%. Comparing the two datasets shows that although the dosage of single Na_2S is approximately 2.7 times the total dosage (2240 g/t) of the quaternary depressant, the Mo grade in the concentrate and the Mo recovery are higher when using the quaternary depressant. According to the calculation of entropy change in Section 2.4, the quaternary depressant obviously has a higher entropy change during the interaction process on the depressed copper mineral surface. This finding confirms that multicomponent depressants have the advantages of low dosage, strong selectivity, and high separation efficiency.

(3) High-entropy activation–flotation.

Activating agents are often used to improve the collection ability and flotation effects of poorly floatable minerals that are difficult to float well using simple collectors alone. Examples include activating zinc sulfide with copper ions in pyrite, lead ions in scheelite, and quartz with calcium ions.

In practical ore activation–flotation, initially, the target mineral requiring activation is identified, with the activating agents selected on the basis of the performance of the subsequent collector, industrial production experience, and previous experimental research results. Then, flotation experi-

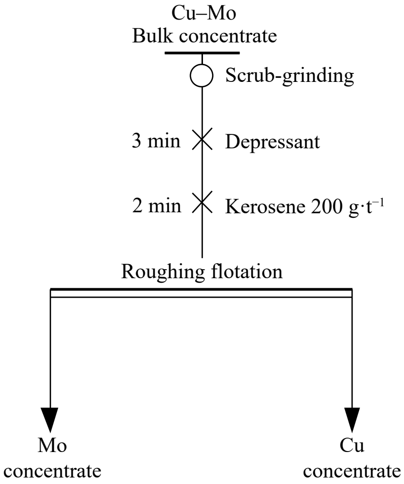

Fig. 8. Flowchart of flotation separation of copper–molybdenum bulk concentrate.

Table 3. Experimental indicators for flotation separation of copper–molybdenum bulk concentrate

Depressants	Dosages / $(g \cdot t^{-1})$	Product	Yield / %	Mo grade		Mo recovery	
				Ind. / %	Cum. / %	Ind. / %	Cum. / %
Na_2S	6000	Mo concentrate	10.54	5.94	5.94	84.33	84.33
		Cu concentrate	89.46	0.13	0.74	15.67	100.00
Na_2S L-cys STG NaDTC	1500 260 180 300	Mo concentrate	8.98	7.22	7.22	87.69	87.69
		Cu concentrate	91.46	0.10	0.74	12.31	100.00

ments are conducted on the selected activating agent to determine its performance, and the type and dosage of the main activating agent are determined. Under the conditions of the main activating agent, the dosage of the auxiliary activating agent is successively examined to determine the agent system of the multicomponent activating agent. The dosage of each activating agent is selected near the determined dosage, and then multifactorial orthogonal experiments are conducted. The optimal system for the activating agent is obtained following verification experiments.

According to the calculational adsorption entropy results for the multicomponent activating agent obtained using Eq. (69), increasing the number of activating agent components considerably increases the adsorption entropy, which improves the stability of the adsorbed activating agent, enhances the adsorption performance of the subsequent collector, and consequently improves the activation–flotation effect for the mineral.

For some heavy metal-ion activating agents, such as Pb^{2+}, Hg^{2+}, and Cd^{2+}, the dosage cannot exceed the maximum amount allowable environmentally, which may affect mineral activation. Some metal-ion activating agents, such as $CuSO_4$, are expensive and require large dosages, resulting in high flotation costs and adverse effects. In such cases, reducing the dosage of the main activating agent and using multicomponent activating agents can increase the adsorption entropy for the activating agent on the mineral surface, thereby enhancing the adsorption capacity and stability of the activating agent and improving the activation–flotation effect for the mineral.

5. Conclusions

On the basis of thermodynamic theory, we systematically and thoroughly studied a complex solid–liquid mineral flotation system, revealing the thermodynamic mechanism associated with the adsorption of flotation reagent components on mineral surfaces and leading to a high-entropy flotation theory and method. The following conclusions are drawn:

(1) The solid–liquid flotation system is thermodynamically isolated, with flotation reagents spontaneously adsorbed on mineral surfaces. The entropy change associated with this process is positive, while the Gibbs free energy change is negative. Multicomponent flotation agents can deliver greater changes in adsorption entropy and smaller changes in adsorption Gibbs free energy than single-component flotation agents, which is the physical essence that underpins the use of multicomponent flotation agents and their synergy to improve flotation efficiency.

(2) We constructed a set of thermodynamic equilibrium equations for a complex solid–liquid mineral flotation system based on the material component, chemical, and phase equilibrium conditions in a solid–liquid flotation system. A change in any component of the pulp solution changes the same component on the mineral surfaces present. The dissolution of a mineral surface component in a pulp solution complicates the pulp solution components while homogenizing various mineral surface components and properties.

(3) The adsorption capacities of the flotation reagents toward the mineral surface increase with flotation reagent concentration in the pulp solution; these reagents are adsorbed on the mineral surface before reaching saturation. The ratio of the adsorption capacity of the mineral surface to the critical adsorption capacity and molar fraction of the residual reagent in the slurry solution is the adsorption equilibrium constant of the flotation reagent. The adsorption equilibrium constant reflects the adsorption abilities and characteristics of the flotation reagents on the mineral surface; it is a basic thermodynamic mineral flotation constant and can be used as an important basis for selecting flotation reagents.

(4) Various collectors, inhibitors, or activators can be combined to improve mineral surface adsorption entropy changes based on a theoretical understanding of the saturation adsorption equilibrium constant for a flotation reagent and the change in the adsorption entropy associated with multicomponent flotation reagents, thereby improving the collection, inhibition, or activation effects of minerals and realizing the efficient flotation recovery of refractory minerals through high-entropy flotation.

Acknowledgements

This work was supported by the Yunnan Science and Technology Leading Talent Project (No. 202305AB350005) and National Science Foundation for Young Scientists of China (No. 51404118).

Conflict of Interest

Shuming Wen is an editorial board member for this journal and was not involved in the editorial review or the decision to publish this article. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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