THERMODYNAMIC ANALYSES FOR S-H$_2$O

SYSTEM AT 25 ℃ [①]

Yi Qingfeng, Chen Qiyuan, Zhang Hengzhong, Zhang Pingmin

Dept. of Chemistry, Central South University of Technology, Changsha 410083

ABSTRACT A new type of potential-pH diagram and distribution curves $X(i)$-pH of aqueous species for the S-H$_2$O system have been reported and discussed according to overall equilibrium principle. The stable region of elemental sulfur is dependent on total sulfur concentration $C_t(S)$ of all species in solution and partial pressure p_{H_2S}/p^0 of H$_2$S gas. When $p_{H_2S}/p^0 = 10^{-6}$ and $C_t(S) = 1$ mol/L, the stable range of sulfur disappears. Dominant region of S$_5^{2-}$ ion in the solution corresponds to stable region of solid sulfur in E_h-pH diagram. This type of E_h-pH diagrams and distribution curves of aqueous species are of both theoretical and practical importance.

Key words potential-pH diagram　thermodynamics　S-H$_2$O system　sulfur

1 INTRODUCTION

Since potential-pH diagrams were established by Pourbaix M, they have been widely used in many fields. There are at present systematical potential-pH diagrams of metal-H$_2$O systems at 25 ℃. It has been generally admitted that thermodynamic changes of these systems can be foreseen through the simple relationship of potential and pH. However, only two substances are considered for each equilibrium line in drawing of Pourbaix diagrams, and the effective concentrations of the two substances are fixed beforehand in order to get exact location of each line. This approach does not match with practical demands in some applications. It has obvious advantages to draw potential-pH diagrams using overall equilibrium principle presented by Congrui F *et al*[1, 2]. The new type of diagrams is different from the old ones and does not have dominant range of each ion (or molecule) , but they have a common solution stable range for all aqueous species. Not only a single ion whose effective concentration is fixed is considered to balance with solid (or gas) phase at the equilibrium line, but all ions in the solution are considered to keep equilibrium with solid (or gas) phase.

The overall equilibrium diagrams of potential-pH in S-H$_2$O system are of importance on theoretical study of the direct electrolysis of aqueous hydrogen sulfide to produce sulfur and hydrogen gas. There is an equilibrium among concentrations of the all species involved in S-H$_2$O system under given values of potential and pH. But such a relationship does not exist in Pourbaix diagrams. So this new type of overall equilibrium diagrams is of both theoretical and practical significance.

In this article, the equilibrium relationships of sulfur and hydrogen sulfide gas with solution will be discussed. The substances here considered are S^{2-}, S$_2^{2-}$, S$_3^{2-}$, S$_4^{2-}$, S$_5^{2-}$, HS$^-$, H$_2$S (aq.), S(s), H$_2$S(g), HSO$_3^-$, SO$_3^{2-}$, HSO$_4^-$, SO$_4^{2-}$, S$_2$O$_3^{2-}$, S$_2$O$_4^{2-}$, S$_2$O$_8^{2-}$, and S$_4$O$_6^{2-}$. Their thermodynamic data are from reference [3]. Other species are not considered because of their insignificant contents.

2 CALCULATION

The species considered in the solution can be divided into two groups for convenient discus-

sion.

(a) species $H_l S_n^{l-2}$: those oxidation states of sulfur element are negtive. For example, when $l = 0$, $H_l S_n^{l-2}$ represents polysulfides or sulfide S_n^{2-} ($n = 1, 2, 3, 4, 5$); when $l = 1$, $H_l S_n^{l-2}$ represents HS^-; when $l = 2$, $H_l S_n^{l-2}$ is H_2S.

(b) species $H_l S_n O_m^{l-2}$: the oxidation states of sulfur element are positive. When $l = 0$, $H_l S_n O_m^{l-2}$ represents SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_4^{2-}$, $S_2O_8^{2-}$; when $l = 1$, $H_l S_n O_m^{l-2}$ represents HSO_3^- and HSO_4^-.

2.1 Overall equilibrium potential-pH diagram

2.1.1 Equilibrium of solid sulfur with solution

The equilibrium potentials of all aqueous species in the solution with respect to sulfur(0) should be the same according to overall equilibrium principle.

(1) Equilibrium of species in group (a) with sulfur

The gerneral electrode reaction can be shown as eqn. (1)

$$H_l S_n^{l-2} = nS(s) + lH^+ + 2e \qquad (1)$$

$[H_l S_n^{l-2}]$ can be expressed as eqn. (2) according to Nernst equation

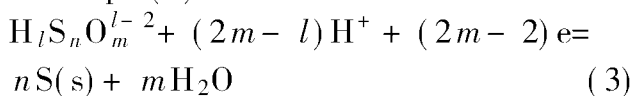$$[H_l S_n^{l-2}] = 10^{(-lpH + (E^0 - E)/0.0295)} \qquad (2)$$

where E^0 is the standard potential of corresponding redox couple $H_l S_n^{l-2}/S$. For example,

$$[S^{2-}] = 10^{(-0.4446 - E)/0.0295} (l = 0, n = 1)$$
$$[HS^-] = 10^{(-pH - 2.119 - 33.898E)}$$
$$(l = 1, n = 1)$$

(2) Equilibrium of species in group (b) with sulfur

The gerneral electrode reaction can be shown as eqn. (3)

$$H_l S_n O_m^{l-2} + (2m - l)H^+ + (2m - 2)e = nS(s) + mH_2O \qquad (3)$$

So, $[H_l S_n O_m^{l-2}]$ can be expressed as eqn. (4) using Nernst equaion

$$[H_l S_n O_m^{l-2}] = 10^{(2m-l)pH + (2m-2)(E - E^0)/0.059} \qquad (4)$$

where E^0 is the standard potentials of corresponding redox couple $H_l S_n O_m^{l-2}/S$.

For example,

$$[HSO_3^-] = 10^{5pH + (E - 0.4759)/0.0148}$$
$$(l = 1, n = 1, m = 3)$$
$$[SO_4^{2-}] = 10^{8pH + (E - 0.3524)/0.00985}$$
$$(l = 0, n = 1, m = 4)$$

The total concentration of sulfur in the solution is denoted as

$$C_t(S) = \Sigma n[H_l S_n O_m^{l-2}] + \Sigma n[H_l S_n^{l-2}] \qquad (5)$$

or

$$\begin{aligned} C_t(S) = {} & [S^{2-}] + 2[S_2^{2-}] + 3[S_3^{2-}] + \\ & 4[S_4^{2-}] + 5[S_5^{2-}] + [HS^-] + \\ & [H_2S(aq.)] + [HSO_3^-] + [SO_3^{2-}] + \\ & [HSO_4^-] + [SO_4^{2-}] + 2[S_2O_3^{2-}] + \\ & 2[S_2O_4^{2-}] + 2[S_2O_8^{2-}] + 4[S_4O_6^{2-}] \end{aligned} \qquad (5')$$

When the items in right hand of eqn. (5') are substituted with corresponding expressions in eqns. (2) and (4), E values can be calculated for given $C_t(S)$ and pH values. Relationship of E and pH is listed in Table 1 when $C_t(S) = 1 mol/L$, and is shown in Fig. 1 or Fig. 2 (curve $s_1 s_2 s_3$).

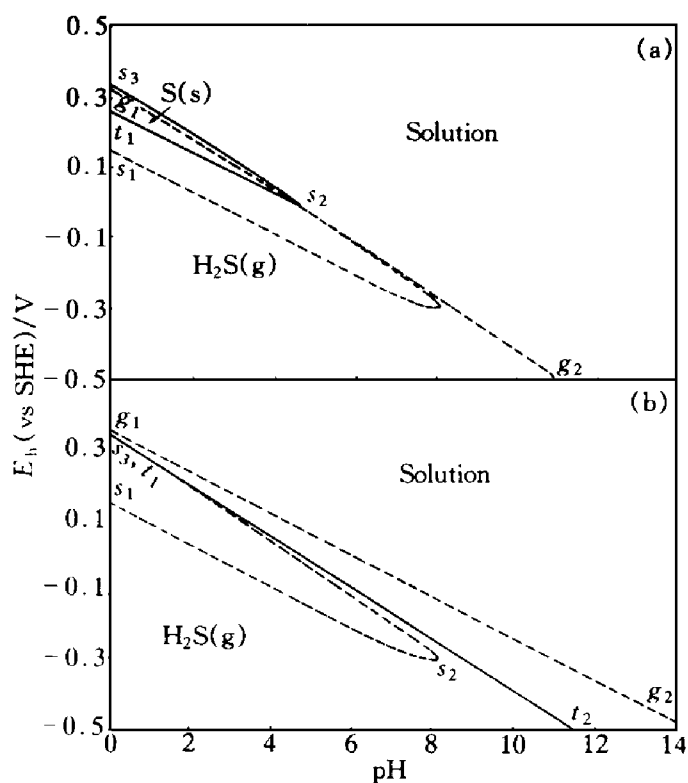### 2.1.2 Equilibrium of H_2S gas with solution

Fig. 1 Effect of $C_t(S)$ on overall equilibrium potential-pH diagram

(25 ℃, $p_{H_2S}/p^0 = 1$)

(a) $-C_t(S) = 1.0 mol/L$; (b) $-C_t(S) = 10 mol/L$
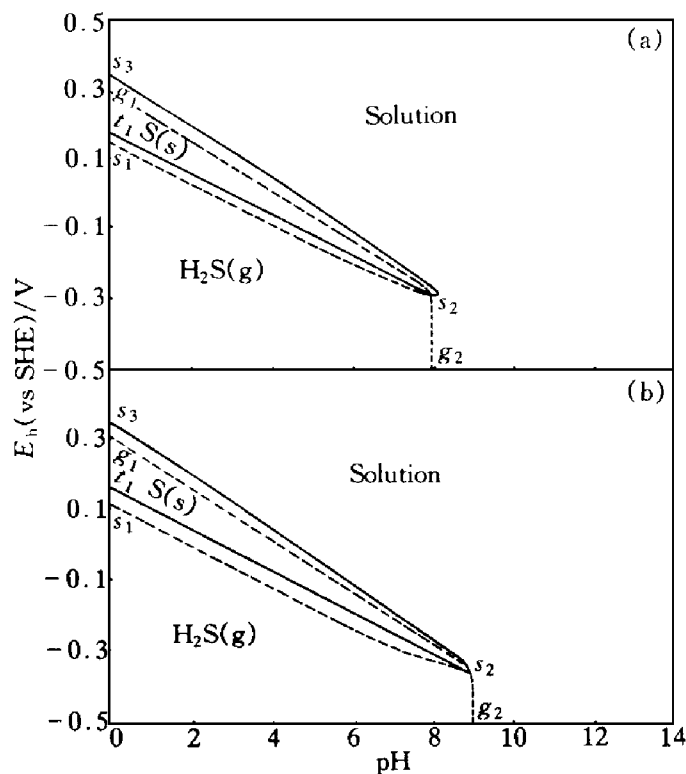
Fig. 2   Effect of p_{H_2S}/p^0 on overall equilibrium potential-pH diagram

(25 ℃, $C_t(S) = 1.0\,mol/L$)

(a) $-p_{H_2S}/p^0 = 0.001$; (b) $-p_{H_2S}/p^0 = 10^{-6}$

**Table 1   Calculated Results According to Eqn. (5)**

pH	E / V		pH	E / V	
– 2	0.265	0.475	6	– 0.205	– 0.125
0	0.145	0.335	8	– 0.295	– 0.275
2	0.025	0.195	8.2	– 0.305	– 0.295
4	– 0.095	0.035			

The equilibrium potentials for all aqueous species in the solution with respect to H$_2$S gas should have a common value according to overall quilibrium principle.
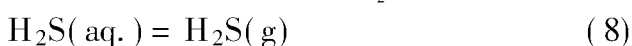
Equilibriums of H$_2$S gas with S^{2-}, HS$^-$ and H$_2$S(aq.) are shown in eqns. (6), (7) and (8).

$$S^{2-} + 2H^+ = H_2S(g) \tag{6}$$
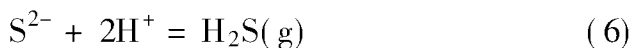
$$[S^{2-}] = 10^{(2pH - 20.91)}(p_{H_2S}/p^0) \tag{6'}$$

$$HS^- + H^+ = H_2S(g) \tag{7}$$
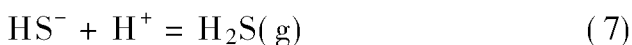
$$[HS^-] = 10^{(pH - 7.995)}(p_{H_2S}/p^0) \tag{7'}$$

$$H_2S(aq.) = H_2S(g) \tag{8}$$

$$[H_2S(aq.)] = 10^{-1.003}(p_{H_2S}/p^0) \tag{8'}$$

The equilibriums of polysulfides S_n^{2-} with H$_2$S gas are

$$S_n^{2-} + 2nH^+ + (2n - 2)e = nH_2S(g)$$
$$(n = 2, 3, 4, 5) \tag{9}$$
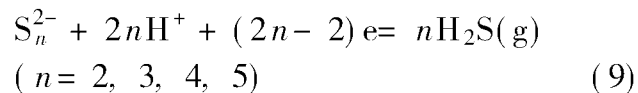
Its Nernst equation is (10):

$$E = E^0 + \{(0.059/(2n - 2))\}\log\{[S_n^{2-}] \times [H^+]^{2n}/(p_{H_2S}/p^0)^n\} \tag{10}$$
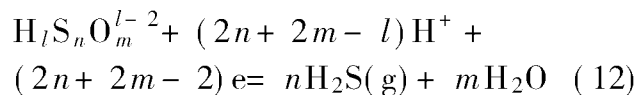
So,

$$[S_n^{2-}] = 10^{2npH+ (n-1)(E- E^0)/0.0295} \times (p_{H_2S}/p^0)^n \tag{11}$$

where E^0 is the standard potential of corresponding redox couple. For example,

$$[S_2^{2-}] = 10^{4pH+ (E- 0.7598)/0.0295} \times (p_{H_2S}/p^0)^2$$
$$(n = 2)$$

The quilibrium of H$_2$S gas with $H_lS_nO_m^{l-2}$ is

$$H_lS_nO_m^{l-2} + (2n + 2m - l)H^+ + (2n + 2m - 2)e = nH_2S(g) + mH_2O \tag{12}$$

Similarly, $[H_lS_nO_m^{l-2}]$ can be expressed as eqn. (13) from its Nernst equation:

$$[H_lS_nO_m^{l-2}] =$$
$$10^{(2n+ 2m- l)pH+ (2n+ 2m- 2)(E- E^0)/0.059} \times (p_{H_2S}/p^0)^n \tag{13}$$

where E^0 is the standard potential of corresponding redox couple $H_lS_nO_m^{l-2}/H_2S(g)$. For example,

$$[HSO_3^-] = 10^{7pH+ (E- 0.3752)/0.00985}(p_{H_2S}/p^0)$$

$$[SO_4^{2-}] = 10^{10pH+ (E- 0.3078)/0.00739}(p_{H_2S}/p^0)$$

The total concentration of sulfur in the solution $C_t(S)$ can be given by eqn. (14), which is similar to eqn. (5):

$$C_t(S) = \Sigma n[H_lS_nO_m^{l-2}] + \Sigma n[H_lS_n^{l-2}] \tag{14}$$

Similarly, E value can be calculated for given pH, $C_t(S)$ and p_{H_2S} according to expressions of (6'), (7'), (8'), (11), and (13). The results are listed in Table 2 for $C_t(S) = 1\,mol/L$ and $p_{H_2S}/p^0 = 1$. The curve of H$_2$S(g)-Soln. is shown in Fig. 1 or Fig. 2(curve g_1, s_2, g_2).

2.1.3   Equilibrium of S-H$_2$S(g)-Solution

Equilibrium potential of sulfur with the solution equals that of $H_2S(g)$ with the solution

Table 2   Calculated results according to Eqn. (16)

pH	E	pH	E
-2	0.425	7.2	-0.235
0	0.295	7.4	-0.255
2	0.145	7.6	-0.265
4	0.005	7.8	-0.285
6	-0.145	7.9	-0.295
7	-0.225		

according to overall equilibrium principle. In other words, the concentration of any aqueous species in balance with sulfur is the same as its concentration in balance with H_2S gas. The following is the result from eqn. (2) ($n=1$) and (6'):

$$(-0.4446 - E)/0.0295 = 2pH - 20.91 + \log(p_{H_2S}/p^0) \quad (15)$$

that is

$$E = 0.1722 - 0.059pH - 0.0295\log(p_{H_2S}/p^0) \quad (15')$$

The corresponding curve of E and pH is shown in Fig. 1(curve t_1s_2) or Fig. 2(b) (curve t_1t_2).

2.2   Distribution of aqueous species composition

Overall equilibrium potential-pH diagram shows dominant regions of solid sulfur, H_2S gas and solution in S-H_2O system. However, it does not indicate directly how the aqueoues species are distributed. Concentrations of the species in the solution can be figured out with overall equilibrium principle.

2.2.1   Equilibrium of polysulfides S_n^{2-} with S^{2-}

The general electrode reaction is

$$S_n^{2-} + (2n-2)e = nS^{2-}$$
$$(n=2, 3, 4, 5) \quad (16)$$
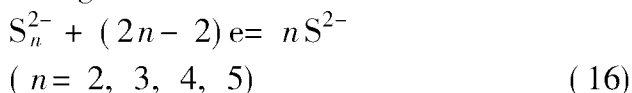
$[S^{2-}]$ can be expressed as eqn. (17) using Nernst equation of (16).

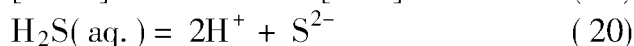$$[S^{2-}] = 10^{(2n-2)(E-E^0)/0.059}[S^{2-}]^n \quad (17)$$

where E^0 is the standard potential of corresponding redox couple S_n^{2-}/S^{2-}.

2.2.2   Equilibrium of HS^- and $H_2S(aq.)$ with S^{2-}

The relationships of $[HS^-]$ and $[H_2S(aq.)]$ with $[S^{2-}]$ can be gotten on the basis of dissociation equilibrium of reactions (18) and (20).
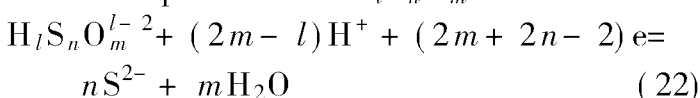
$$HS^- = H^+ + S^{2-} \quad (18)$$
$$[HS^-] = 10^{(12.91-pH)}[S^{2-}] \quad (19)$$
$$H_2S(aq.) = 2H^+ + S^{2-} \quad (20)$$
$$[H_2S(aq.)] = 10^{(19.90-2pH)}[S^{2-}] \quad (21)$$

2.2.3   Equilibrium of $H_lS_nO_m^{l-2}$ with S^{2-}

$$H_lS_nO_m^{l-2} + (2m-l)H^+ + (2m+2n-2)e = nS^{2-} + mH_2O \quad (22)$$
$$[H_lS_nO_m^{l-2}] = 10^{(2m-l)pH+(2m+2n-2)(E-E^0)/0.059}[S^{2-}]^n \quad (23)$$

where E^0 is the standard potential of the corresponding redox couple $H_lS_nO_m^{l-2}/S^{2-}$.

The total sulfur concentration of aqueous species is denoted as $C_t(S)$, then

$$C_t(S) = \Sigma n[Sn^{2-}] + [HS^-] + [H_2S(aq.)] + \Sigma n[H_lS_nO_m^{l-2}] \quad (24)$$

The ratio $X(i)$ of the total sulfur concentration of species i to that of all species in the solution can be expressed as follows:

$$X(i) = g[i]/C_t(S) \quad (25)$$

where g is sulfur atom numbers in species i. Relationships of $X(i)$ and pH for given values of potentials and $C_t(S)$ are shown in Figs. 3 and 4.

3   RESULTS AND DISCUSSION

Potential-pH diagrams can be constructed for given pH, $C_t(S)$ and p_{H_2S}/p^0, according to eqns. (5), (14) and (15), and they are shown in Figs. 1 and 2. The Figs. show that there is only one common stable range for all aqueous species, being different from Pourbaix diagrams. In Fig. 1 and Fig. 2(a), the region around solid curves t_1s_2 and s_2s_3 is stable range of sulfur, the region around curves t_1s_2 and s_2g_2 is that of H_2S gas, and other is that of aqueoues species. Figs.

1 and 2 show that stable regions of solid sulfur and H$_2$S gas are dependent on both total content C_t(S) and partial pressure of H$_2$S gas. Figs. 3 and 4 show the relationships of the species in solution and C_t(S) or potentials.
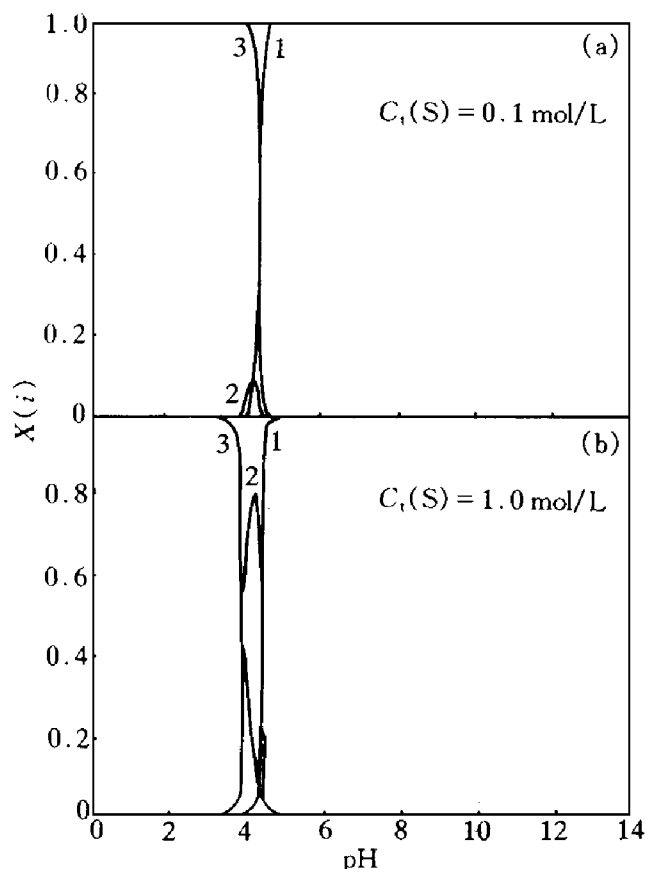
but that of H$_2$S gas increases, with the decreasing of p_{H_2S}/p^0. When p_{H_2S}/p^0 decreases, anodic potentials increases, and so does concentration of higher valent sulfur species in the solution. When $p_{H_2S}/p^0 = 10^{-6}$, the stable region of elemental sulfur disappears because locations of curves s_1s_2 and s_2s_3 are not dependent upon p_{H_2S}/p^0 (seeing Figs. 1 and 2). Fig. 2(b) shows that the range below curve g_1g_2 is stable region of H$_2$S gas.
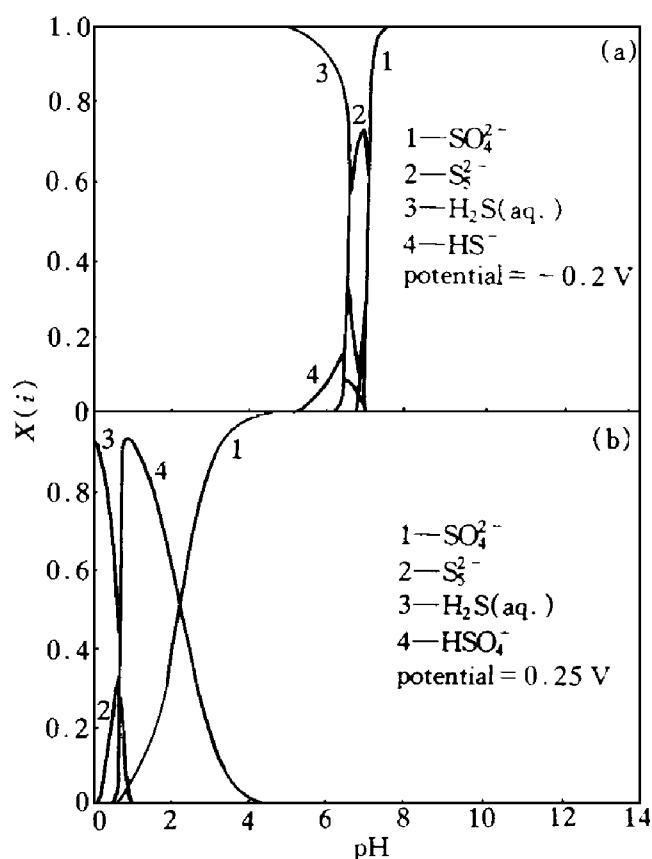
Fig. 3   Effect of C_t(S) on distribution diagrams (potential= 0 V)
1 —SO$_4^{2-}$; 2 —S$_5^{2-}$; 3 —H$_2$S(aq.)

Fig. 4   Effect of potentials on distribution diagrams (C_t(S)= 1. 0 mol/ L)

3. 1   Effect of C_t(S) on E_h-pH diagrams

Fig. 1 shows that the region around curves s_1s_2 and s_2s_3 becomes bigger with increasing C_t(S). Howerver, three-phase line t_1s_2 is not associated with C_t(S). So the extent that stable region of solid sulfur increases with C_t(S) is not very obvious. The stable region of hydrogen sulfide gas also increases and shifts to the solution of higher pH.

3. 2   Effect of p_{H_2S}/p^0 on E_h-pH diagrams

Fig. 2 shows that the effect of p_{H_2S}/p^0 is greater than that of C_t(S). When C_t(S) is fixed, stable region of sulfur becomes narrower,

As can be seen from the discussion above that the presence of H$_2$S gas has great effect on stable region of sulfur. When C_t(S) of aqueous species in solution and p_{H_2S}/p^0 of H$_2$S gas increase, the stable region of elemental sulfur becomes wider and longer, which favours electrolytical oxidation of low oxidate numbers species, such as H$_2$S(aq.), HS$^-$ et al, to produce sulfur.

3. 3   Distribution curve diagrams

Figs. 3 and 4 show that dominant species in

the solution are S_5^{2-}, $H_2S(aq.)$, HS^-, HSO_4^-, and SO_4^{2-}, in the range of potentials considered here. Considerable amount of SO_4^{2-} ion is present even in acidic solution with increasing potentials. SO_4^{2-} ion is also dominant in alkaline solution at more negative potentials. In other words, SO_4^{2-} ion is stable thermodynamically in wider ranges of potentials and pH. $H_2S(aq.)$ is present only in a strong acidic solution when potential is 0. 25V. HS^- ion only exists in the vicinity of neutral solution. Distribution curves of S_5^{2-} ion progressively shift to acidic solution with increasing potentials. Figs. 3 and 4 also show that S_5^{2-} ion is present in the corresponding solution of sulfur stable region in E_h-pH diagram. $X(S_5^{2-})$ decreases with the increasing of potentials, this is due to oxidation of S_5^{2-} at higher potentials.

$$S_5^{2-} + 20H_2O = 5SO_4^{2-} + 40H^+ + 32e \quad (26)$$
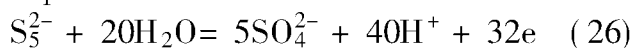
Effect of $C_t(S)$ on $X(S_5^{2-})$ is shown in Fig. 3. $X_{max}(S_5^{2-})$ increases with $C_t(S)$. When $C_t(S)$ changes from 0. 1 to 1. 0 mol/ L, $X_{max}(S_5^{2-})$ increases from 0. 1 to 0. 8. So continuous increasing $C_t(S)$ has not great effect on content of S_5^{2-} ion in the solution. Because polysulfides are intermediates during electrolysis of sulfides to produce sulfur[4], it is important how aqueous species, especially polysulfides, are distributed with $C_t(S)$ and potentials.

4 CONCLUSION

Thermodynamic analyses for the sulfur-water system indicate that overall equilibrium potential pH diagrams consist of three phases, i. e. solid sulfur, aqueous species and hydrogen sulfide gas, and that the domiant species in the solution are SO_4^{2-}, HSO_4^{2-}, $H_2S(aq.)$, HS^-, and S_5^{2-}. Both the stable region of elemental sulfur and distributions of S_5^{2-} ion concentrations with pH are dependent on total sulfur content $C_t(S)$ of aqueous species. Partial pressures of H_2S gas have great effects on stable regions of sulfur.

REFERENCES

1   Fu Chongyue, Zheng Diji, J. Cent South Inst Min Metall, (in Chinese), 1979, (1): 27.
2   Luo Rutie. Hydrometallurgy, 1987, 17: 177.
3   Donald D W, William H E, Vivian B P et al. NBS Table of Chemical Thermodynamic Properties. New York: the American Chemical Society and the American Institute of Physics for the NBS, 1983.
4   Buckley A N, Hamilton I C, Woods R. J Electroanal Chem, 1987, 216: 213.

(Edited by Wu Jiaquan)