

# POTENTIAL-pH DIAGRAMS OF Al-H<sub>2</sub>O SYSTEM<sup>①</sup>

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**ABSTRACT** The known thermodynamic data for Al-H<sub>2</sub>O system have been summarized and evaluated. The high temperature thermodynamic data of some ions have also been obtained by combining the entropy of ions at 298 K with the extrapolation method of Criss and Cobble. Using these data, potential-pH diagrams of Al-H<sub>2</sub>O system at both 298 and 363 K have been presented, respectively.

**Key words** Al-H<sub>2</sub>O system potential-pH diagram thermodynamics

## 1 INTRODUCTION

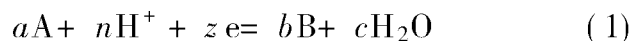
Knowledge of the chemistry of aqueous solutions has advanced rapidly, with the accumulation of large quantities of theoretical and experimental thermodynamic data. The potential-pH diagram developed by Pourbaix<sup>[1]</sup> plays an important role in the investigation of solution thermodynamics and has been widely used in hydrometallurgy, metal corrosion, water purification, geochemistry, analytical chemistry and electrochemistry<sup>[2, 3]</sup>.

Few studies have been reported on potential-pH diagrams of Al-H<sub>2</sub>O system at ambient temperature, especially at high temperatures for lack of thermodynamic data of some species. Potential-pH diagrams of Al-H<sub>2</sub>O system are of important practical value for improvement of Bayer's process in the industrial production of alumina and the investigation of corrosion behavior of aluminum alloy. In addition, it also provides a certain guide for recent studies on the hydrolysis process of aluminum ion in the preparation of ultrafine alumina powder from aluminum inorganic salt<sup>[4, 5]</sup>.

The known thermodynamic data for Al-H<sub>2</sub>O system were summarized, evaluated, and calculated in the present work, and using these data, potential-pH diagrams of Al-H<sub>2</sub>O system at both 298 and 363 K were presented, respectively.

## 2 THERMODYNAMIC DATA

Table 1 summarizes the thermodynamic data for various species that were used in the derivation of the potential-pH diagrams at 298 K, including the standard molar Gibbs free energy of formation ( $\Delta_f G_m^0$ ), standard molar enthalpy of formation ( $\Delta_f H_m^0$ ) and standard molar entropy ( $S_m^0$ ). The thermodynamic data of Al(OH)<sub>3</sub>(s) (gibbsite), AlOOH(s) (boehmite), Al<sup>3+</sup>(aq) and Al(OH)<sub>4</sub><sup>-</sup>(aq) coming from literatures [6–12] are so far comparatively reliable and consistent ones. Other thermodynamic data in Table 1 come from CODATA Key Values<sup>[13]</sup>. The equilibrium equations involving the species listed in Table 1 are shown in Table 2. These equations have a general form:



Assuming that the activities of Al<sup>3+</sup>(aq), Al(OH)<sub>4</sub><sup>-</sup>(aq) and all solid phases are all equal to 1, and the pressures of both H<sub>2</sub>(g) and O<sub>2</sub>(g) are  $1.0 \times 10^5$  Pa, the potentials or pH values of different reactions in Table 2 can be computed by using the thermodynamic data of Table 1.

## 3 POTENTIAL ( $\varphi_T^0$ ) AND pH<sub>T</sub><sup>0</sup> AT EVALUATED TEMPERATURES

For any reaction, the Gibbs free energy

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change at any temperature  $T$  can be expressed as:

$$\Delta G_T^0 = \Delta G_{298}^0 - \Delta S_{298}^0 (T - 298.15) + \int_{298.15}^T \Delta C_p^0 dT - T \int_{298.15}^T \Delta C_p^0 d(\ln T) \quad (2)$$

If the heat capacity change of any reaction ranging from 298 K to  $T$  is regarded as a constant  $\Delta C_p^0|_{298}$ , then:

$$\Delta G_T^0 = \Delta G_{298}^0 - \Delta S_{298}^0 (T - 298.15) + \Delta C_p^0|_{298} [ (T - 298.15) - T \ln T / 298.15 ] \quad (3)$$

According to reaction (3),  $\varphi_T^0$  for an oxidat

tion-reduction reaction at any temperature is given by:

$$\varphi_T^0 = \varphi_{298}^0 + (T - 298.15) \Delta S_{298}^0 / Fz - [ (T - 298.15) - T \ln T / 298.15 ] \Delta C_p^0|_{298} / Fz \quad (4)$$

where  $F$  is the Faraday's constant and  $z$  is the electron transfer number.

The  $\text{pH}_T^0$  for a dissolution-precipitation reaction can be written as:

$$\text{pH}_T^0 = 298.15 \text{pH}_{298}^0 / T + (T - 298.15) \Delta S_{298}^0 / 2.303 nRT - [ (T - 298.15) - T \ln T / 298.15 ] \Delta C_p^0|_{298} / 2.303 nRT \quad (5)$$

where  $n$  is the number of  $\text{H}^+$  (aq) participating in the reaction.

From Eqns. (4) and (5) it can be seen that the relationships between molar heat capacity and temperature of various species must be obtained in order to acquire  $\varphi_T^0$  and  $\text{pH}_T^0$ . The relations between molar heat capacity and temperature of  $\text{Al}(\text{OH})_3(\text{s})$  (gibbsite) and  $\text{AlOOH}(\text{s})$  (boehmite) can be found from literatures [10, 12], while those of  $\text{Al}(\text{s})$ ,  $\text{H}_2\text{O}(\text{s})$ ,  $\text{O}_2(\text{s})$  and  $\text{H}_2(\text{s})$  can be taken from literature [14].

Hovey and Tremaine<sup>[15]</sup> calorimetrically determined the molar heat capacity of  $\text{Al}^{3+}(\text{aq})$  at temperatures 283~328 K as:

$$C_p^0 = 566.2 - 1.452T - 27338/T - 190 \quad (6)$$

Hovey and Hepler<sup>[16]</sup>, Caiani *et al*<sup>[17]</sup> and Chen *et al*<sup>[18]</sup> measured the molar heat capacity data at different temperatures using calorimetric method. After comprehensive treatment, we have:

$$C_p^0 = -1040.768 + 6.329143T - 8.498212 \times 10^{-3} T + 224.2222 / (T - 470), \quad 298 \sim 433 \text{ K} \quad (7)$$

The high temperature heat capacities of  $\text{H}^+(\text{aq})$  can be obtained by extrapolation method of Criss and Cobble<sup>[19]</sup>.

## 4 RESULTS AND DISCUSSION

Equations describing the equilibria of Table 2 can be used to construct a number of potential-

**Table 1 Thermodynamic data of main species of Al-H<sub>2</sub>O system at 298 K**

Species	$-\Delta_f G_m^0$ / kJ•mol <sup>-1</sup>	$-\Delta_f H_m^0$ / kJ•mol <sup>-1</sup>	$\Delta S_m^0$ / J•mol <sup>-1</sup> •K <sup>-1</sup>
Solid species			
Al(s)	0 <sup>1)</sup>	0	28.30
Al(OH) <sub>3</sub> (s) (gibbsite)	1155.05	1293.18	68.44
AlOOH(s) (boehmite)	918.15	996.10	37.19
Dissolved species			
Al <sup>3+</sup> (aq)	488.69	538.25	-333.78
Al(OH) <sub>4</sub> <sup>-</sup> (aq)	1305.29	1503.65	99.51
Aqueous species			
H <sub>2</sub> O(l)	237.189	285.830	69.95
H <sup>+</sup> (aq)	0 <sup>1)</sup>	0	0
OH <sup>-</sup> (aq)	157.269	230.015	-10.90
Gaseous species			
O <sub>2</sub> (g)	0 <sup>1)</sup>	0	205.043
H <sub>2</sub> (g)	0 <sup>1)</sup>	0	130.571

1) Defined reference state.

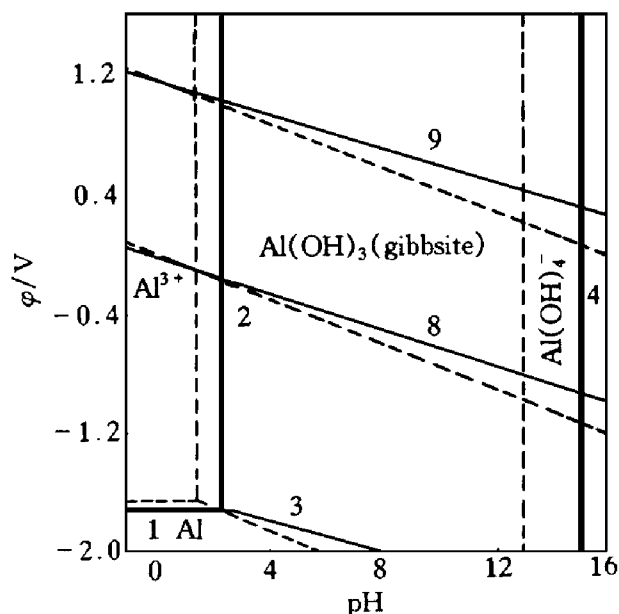
**Table 2 Reactions between species of Al-H<sub>2</sub>O system**

No.	Reactions
1	$\text{Al}^{3+} + 3\text{e} = \text{Al}$
2	$\text{Al}(\text{OH})_3 + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$
3	$\text{Al}(\text{OH})_3 + 3\text{H}^+ + 3\text{e} = \text{Al} + 3\text{H}_2\text{O}$
4	$\text{Al}(\text{OH})_3 + \text{H}_2\text{O} = \text{Al}(\text{OH})_4^- + \text{H}^+$
5	$\text{AlOOH} + 3\text{H}^+ = \text{Al}^{3+} + 2\text{H}_2\text{O}$
6	$\text{AlOOH} + 3\text{H}^+ + 3\text{e} = \text{Al} + 2\text{H}_2\text{O}$
7	$\text{AlOOH} + 2\text{H}_2\text{O} = \text{Al}(\text{OH})_4^- + \text{H}^+$
8	$2\text{H}^+ + 2\text{e} = \text{H}_2$
9	$1/2\text{O}_2 + 2\text{H}^+ + 2\text{e} = \text{H}_2\text{O}$

Note: The states of various species are obvious.

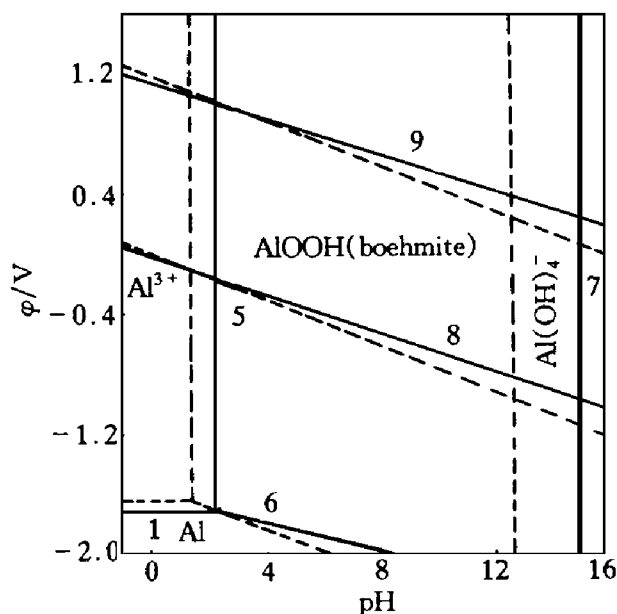
pH diagrams. The potential-pH diagrams of  $\text{Al-H}_2\text{O}$  system at 298 and 363 K are shown in Figs. 1 and 2, separately. The number of each line in Figs. 1 and 2 responds to one of the various equilibrium reactions in Table 2.

Fig. 1 shows the predominances of  $\text{Al}^{3+}$



**Fig. 1 Potential-pH diagram of  $\text{Al-H}_2\text{O}$  system**

(responding to reactions 1, 2, 3, 4, 8, 9)  
solid line—298 K; dashed line—363 K



**Fig. 2 Potential-pH diagram of  $\text{Al-H}_2\text{O}$  system**

(responding to reactions 1, 5, 6, 7, 8, 9)  
solid line—298 K; dashed line—363 K

(aq) at  $\text{pH} < 2.64$ ,  $\text{Al}(\text{OH})_3(\text{gibbsite})$  at  $2.64 < \text{pH} < 12.95$  and  $\text{Al}(\text{OH})_4^-$  (aq) at  $\text{pH} > 12.95$  when the temperature is 298 K. It also shows that  $\text{Al}^{3+}$  (aq) becomes the predominant species at  $\text{pH} < 1.59$ , so does  $\text{Al}(\text{OH})_3(\text{gibbsite})$  at  $1.59 < \text{pH} < 12.95$  and  $\text{Al}(\text{OH})_4^-$  (aq) at  $\text{pH} > 12.95$  when the temperature rises to 363 K. It can be seen that the line boundaries move in the direction of lower pH values with increasing temperature. In particular, the effect is more pronounced at high pH values, with a dramatic expansion of the region of predominance of the hydrolysis species  $\text{Al}(\text{OH})_4^-$  (aq) and a consequent decrease in the domain of  $\text{Al}(\text{OH})_3(\text{gibbsite})$  compared with that at 298 K.

Fig. 2 indicates that  $\text{Al}^{3+}$  (aq) becomes the predominant species at  $\text{pH} < 2.62$ , so do  $\text{AlOOH}(\text{boehmite})$  at  $2.62 < \text{pH} < 12.58$  and  $\text{Al}(\text{OH})_4^-$  (aq) at  $\text{pH} > 12.58$  when the temperature is 298 K. It also indicates the predominances of  $\text{Al}^{3+}$  (aq) at  $\text{pH} < 1.48$ ,  $\text{AlOOH}(\text{boehmite})$  at  $1.48 < \text{pH} < 12.55$  and  $\text{Al}(\text{OH})_4^-$  (aq) at  $\text{pH} > 12.55$  when the temperature is 363 K. It can be seen that the line boundaries move in the direction of lower pH values with increasing temperature. Especially, the effect is more pronounced at high pH values, with an obvious expansion of the region of predominance of the hydrolysis species  $\text{Al}(\text{OH})_4^-$  (aq) and a consequent decrease in the domain of  $\text{AlOOH}(\text{boehmite})$  compared with that at 298 K.

Apps *et al.*<sup>[20]</sup> measured the solubilities of  $\text{Al}(\text{OH})_3(\text{gibbsite})$  and  $\text{AlOOH}(\text{boehmite})$  at different pH values, whose stability regions are basically consistent with those in Figs. 1 and 2, respectively.

It can also be seen from Figs. 1 and 2 that the hydrolysis of  $\text{Al}^{3+}$  (aq) produces either  $\text{Al}(\text{OH})_3(\text{gibbsite})$  or  $\text{AlOOH}(\text{boehmite})$ . But, this is only a possibility. What the products of hydrolysis of  $\text{Al}^{3+}$  (aq) actually are needs to be confirmed by further kinetic investigation.

## 5 CONCLUSION

In summary, the potential-pH diagrams of

$Al-H_2O$  system developed in this work provide a direct description for various possible equilibria in the aqueous system, and a certain guide for the improvement of Bayer's process in the industrial production of alumina, the investigation of corrosion behavior of aluminum alloy and the preparation of alumina materials.

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