Oxidation of As(III) with Dissolved Molecular Oxygen in Alkaline Solutions*

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The kinetics of the oxidation reaction of As(III) with dissolved molecular oxygen in alkaline solutions was investigated. The oxidation rate of As(III) obeys the equation,

$$R = k'_2 \cdot C_{\text{As(III)}} \cdot p_{\text{O}_2} \cdot a_{\text{MOH}},$$

in aqueous NaOH and KOH solutions. The principal rate determining step in this oxidation reaction appears to be a chemical reaction process. Support of this analysis lies in an apparent activation energy of $73.2 \text{ kJ} \cdot \text{mol}^{-1}$ and reaction rates independent of the agitation speed. The oxidation rates of As(III) increased in various alkaline solutions according to the sequence of $\text{KOH} < \text{NaOH} < \text{LiOH}$. This sequence coincides with the amount of free water available in the solutions. Also, the accumulation of As(V) tends to suppress the reaction slightly.

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I. Introduction

In the purification process of zinc hydrometallurgy, the cementation method using arsenous acid and zinc powder is widely utilized. In connection to the pollution control of arsenic compounds, some novel methods have been proposed for recycle of arsenous acid⁽¹⁾⁽²⁾. These processes involve recovering arsenic compounds by oxidizing As(III) in alkaline solutions with dissolved molecular oxygen, followed by the separation of As(V) from copper compounds. Thus, the As(V) compounds are recovered as arsenous acid or zinc arsenate.

Arsenic is a common element and usually contained in sulfide ores. A number of attempts have been made to fix arsenic in various forms during metallurgical processes. However, Robins recently pointed out that the solubilities of various arsenic compounds increase under the action of carbon dioxide con-

tained in air⁽³⁾, and thus it is necessary to pay a particular caution to their pollution control. In the purification of arsenic compounds, the oxidation reaction of As(III) with dissolved molecular oxygen is thought to be important. In acidic solutions the oxidation of As(III) with oxygen is very slow even at elevated temperatures and under oxygen pressure. In alkaline solutions, the oxidation reaction of As(III) is still slow, but it is promoted greatly with rising temperature and increasing oxygen partial pressure.

The mechanisms of oxidation reactions of As(III) by ozone⁽²⁾, hydrogen peroxide⁽³⁾ and ferricyanide ions⁽⁴⁾⁽⁵⁾ were investigated previously. Results of a kinetic study of As(III) oxidation with dissolved molecular oxygen⁽⁶⁾ indicate that the oxidation rate under pressurized oxygen is of the first order with respect to As(III) concentration. However, no other study has been reported.

The elucidation of oxidation mechanism of As(III) with dissolved molecular oxygen is not only of an academic interest but also of an industrial value. This paper describes results obtained in the kinetic study of oxidation reaction of As(III) with dissolved molecular oxygen in alkaline solutions.

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II. Experimental Procedures

A $1 \times 10^{-3} \text{ m}^3$ glass autoclave was used as a reactor for oxidation experiments at higher oxygen pressures. After a test solution of $5 \times 10^{-4} \text{ m}^3$ was charged in the autoclave, the reactor was sealed. During temperature regulation, the solution was agitated with a Teflon blade. When the temperature reached a predetermined level, agitation was stopped and the oxygen gas was introduced to a definite pressure. The experiment was initiated when the agitation was re-started. During the experiment, the oxygen partial pressure was kept constant unless otherwise stated. An agitation speed at 16.7 s^{-1} was maintained throughout the experiment.

Sample solutions, 10 cm^3 each, were taken at predetermined intervals, and the concentration of As(III) in the sample solution was determined by oxidative titration with potassium bromate to obtain a rate curve.

Solutions of As(III) and As(V) were prepared by dissolving reagent grade As_2O_3 and As_2O_5 in NaOH solutions of known concentrations. Other chemicals used in this study were of reagent grade. De-ionized water with specific conductivity lower than $2 \times 10^{-5} \text{ S} \cdot \text{m}^{-1}$ was used in preparation of the solutions.

III. Experimental Results and Discussion

Loehr and Plane⁽⁷⁾ suggested that the species of As(III) in alkaline solutions are $\text{As}(\text{OH})_3$, $\text{AsO}(\text{OH})_2^-$, $\text{AsO}_2(\text{OH})^{2-}$ and AsO_3^{3-} . Ionization constants of $\text{As}(\text{OH})_3$, i.e. H_3AsO_3 , were reported to be $pK_{a_1}=9.1$, $pK_{a_2}=12.1$ and $pK_{a_3}=13.4$ at 298 K ⁽⁸⁾. Pourbaix⁽⁹⁾ and Charlott⁽¹⁰⁾ noted that the stable species of As(III) in alkaline solution was AsO_2^- , which was equivalent to the dehydrated species of $\text{AsO}(\text{OH})_2^-$ mentioned above. Yet, it is known that $\text{AsO}(\text{OH})_3$, $\text{AsO}_2(\text{OH})_2^-$, $\text{AsO}_3(\text{OH})^{2-}$ and AsO_4^{3-} exist in alkaline solutions as the species of As(V). The acidic ionization constants of H_3AsO_4 equivalent to $\text{AsO}(\text{OH})_3$ were reported to be $pK_{a_1}=2.2$, $pK_{a_2}=7.0$ and $pK_{a_3}=11.5$ at 298 K ⁽¹¹⁾. The concentrations of alkali studied in this work ranged from 0.5 to $5 \text{ kmol} \cdot \text{m}^{-3}$,

and thus the overall oxidizing reaction of As(III) by pressurized oxygen should differ with pH. However, the overall reaction may be expressed by either eq. (1) or (2).

Reaction (1) consumes OH^- , and as a result of oxidation, AsO_3^{3-} ions in the solution are converted to HASO_3^{2-} .

Figure 1 shows typical reaction rates for the oxidation of As(III) under various experimental conditions, $\ln C_{\text{As(III)}}$ being plotted against time. The initial $C_{\text{As(III)}}$ in these experiments was kept constant at $5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$. The measured rates were located on each straight line except at earlier and later stages of oxidation reaction under all experimental conditions studied. This fact suggests that the reaction rate is of the first order with respect to As(III) concentration. The first order dependence was supported by the fact that plots of other orders did not fit the measured rates. The deviation from the straight line observed at the initial stage of reaction tended to increase when the reaction rate was high. It might be thought

Fig. 1 Typical reaction rates for the oxidation of As(III) under various conditions: $C_{\text{As(III)}} 5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$, $p_{\text{O}_2} 5.1 \times 10^5 \text{ Pa}$, $\omega 16.7 \text{ s}^{-1}$.

- A: $C_{\text{NaOH}} 0.5 \text{ kmol} \cdot \text{m}^{-3}$, Temp. 383 K .
- B: $C_{\text{NaOH}} 3 \text{ kmol} \cdot \text{m}^{-3}$, Temp. 343 K .
- C: $C_{\text{KOH}} 1.5 \text{ kmol} \cdot \text{m}^{-3}$, Temp. 383 K .
- D: $C_{\text{NaOH}} 1.5 \text{ kmol} \cdot \text{m}^{-3}$, Temp. 383 K .
- E: $C_{\text{LiOH}} 1.5 \text{ kmol} \cdot \text{m}^{-3}$, Temp. 383 K .
- F: $C_{\text{NaOH}} 5 \text{ kmol} \cdot \text{m}^{-3}$, Temp. 343 K .
- G: $C_{\text{NaOH}} 4 \text{ kmol} \cdot \text{m}^{-3}$, Temp. 363 K .

that the oxidation of As(III) with oxygen originally present in the reaction vessel before the start of oxidation experiment caused the initial stage deviation. This explanation is plausible, since the amount of As(III) pre-oxidized was always smaller stoichiometrically than that of oxygen originally present in the reaction vessel. On the other hand, it should be considered that the As(V) formed is one of the factors affecting the deviation from the straight line observed at the later stages of oxidation reaction.

Therefore, the effect of As(V) present in the solution on the oxidation of As(III) in NaOH solution was examined. As shown in Fig. 2, the oxidation rates of As(III) in NaOH solution containing an amount of As(V) equivalent to or excessive over As(III) decreased distinctly with the increase in As(V) concentration. The oxidation reaction of As(III) was retarded by the addition of As(V), but the first order dependence of oxidation rate upon As(III) concentration was maintained.

These observations indicate that the deviation from the first order plots observed at the later stage of oxidation reaction is caused by the As(V) formed by the oxidation reaction.

Fig. 2 Effect of As(V) on reaction rates of the oxidation of As(III) in NaOH solutions: $C_{\text{As(III)}} 5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$, $p_{\text{O}_2} 5.1 \times 10^5 \text{ Pa}$, $\omega 16.7 \text{ s}^{-1}$.
 A: $C_{\text{NaOH}} 1 \text{ kmol} \cdot \text{m}^{-3}$, $C_{\text{As(V)}} 0$, Temp. 383 K.
 B: $C_{\text{NaOH}} 1 \text{ kmol} \cdot \text{m}^{-3}$, $C_{\text{As(V)}} 5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$, Temp. 383 K.
 C: $C_{\text{NaOH}} 1 \text{ kmol} \cdot \text{m}^{-3}$, $C_{\text{As(V)}} 2 \times 10^{-1} \text{ kmol} \cdot \text{m}^{-3}$, Temp. 383 K.
 D: $C_{\text{NaOH}} 4 \text{ kmol} \cdot \text{m}^{-3}$, $C_{\text{As(V)}} 0$, Temp. 343 K.
 E: $C_{\text{NaOH}} 4 \text{ kmol} \cdot \text{m}^{-3}$, $C_{\text{As(V)}} 5 \times 10^{-2}$ or $2 \times 10^{-1} \text{ kmol} \cdot \text{m}^{-3}$, Temp. 343 K.

Therefore, the reaction rate constant defined by eq. (3) was determined for each experiment, to examine various factors which might affect oxidation rates, using the following equation:

$$R = -\frac{dC_{\text{As(III)}}}{dt} = k'_1 \cdot C_{\text{As(III)}}, \quad (3)$$

where k'_1 is an apparent rate constant, which can be determined from the slope of linear portion in the plots of $\ln C_{\text{As(III)}}$ against reaction time.

The effect of oxygen partial pressure on the oxidation rate of As(III) in $1 \text{ kmol} \cdot \text{m}^{-3}$ NaOH was examined at 363 K. The results in Fig. 3 show a satisfactory linear relationship between k'_1 and oxygen partial pressure. Hence, the oxidation rate can be described by eq. (4),

$$R = k_1 \cdot C_{\text{As(III)}} \cdot p_{\text{O}_2}, \quad (4)$$

where k_1 denotes an apparent rate constant having a dimension of $\text{s}^{-1} \cdot \text{Pa}^{-1}$.

The oxidation rates of As(III) are significantly influenced by the concentration of alkali used, as is obvious from Fig. 1. A further examination was made to elucidate the role of alkali in the oxidation reaction of As(III) with dissolved molecular oxygen. In these experiments, $C_{\text{As(III)}}$ and p_{O_2} were kept constant at $5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$ and $5 \times 10^5 \text{ Pa}$, respectively, and the concentrations of NaOH, KOH and LiOH were changed from 0.5 to $5 \text{ kmol} \cdot \text{m}^{-3}$. The results are shown in Fig. 4, in which k_1 was plotted against C_{MOH} . The oxidation rates increased greatly with the increase in alkali con-

Fig. 3 Effect of oxygen partial pressure on reaction rates: $C_{\text{As(III)}} 5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$, $C_{\text{NaOH}} 1 \text{ kmol} \cdot \text{m}^{-3}$, Temp. 363 K, $\omega 16.7 \text{ s}^{-1}$.

Fig. 4 Effect of the concentration of alkalis on reaction rates: $C_{\text{As(III)}} 5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$, $p_{\text{O}_2} 5.1 \times 10^5 \text{ Pa}$, $\omega 16.7 \text{ s}^{-1}$. $\circ$ NaOH system, Temp. 343 K. $\bullet$ NaOH system, Temp. 363 K. $\odot$ NaOH system, Temp. 383 K. $\triangle$ KOH system, Temp. 383. $\square$ LiOH system, Temp. 383 K.

centration for all alkalis studied. For example, the oxidation rates of As(III) in NaOH solutions at 363 K exhibit apparently the fourth order dependence at NaOH concentrations above $3 \text{ kmol} \cdot \text{m}^{-3}$. However, the dependence of oxidation rates upon alkali concentration in dilute alkali solutions appeared to be less significant. A similar tendency was observed for alkalis other than NaOH, and the absolute values of oxidation rates largely depend on the alkalis used. A comparison between the k_1 values for three alkalis at the same C_{MOH} showed that the oxidation reaction of As(III) in LiOH was the fastest, while that in KOH was the slowest.

This study demonstrates that the role of alkali in the oxidation reaction of As(III) is complex as already mentioned. In this regard, we previously found in a study dealing with the oxidation of Fe(II) in HCl solutions with dissolved molecular oxygen, that the HCl activity, not the HCl concentration, is a direct rate controlling factor⁽¹²⁾. In the present study, the applicability of a similar method was examined to clarify the role of alkali in the As(III) oxidation reaction.

The data of Fig. 4 were re-plotted against a_{MOH} . The values of activities of NaOH, KOH and LiOH at 298 K are available in the literature. No available data of a_{MOH} at elevated temperatures have been reported. However, the temperature dependence of mean activity coefficients of aqueous solutions of NaOH or KOH was studied by Åkerlöf and his co-workers at the temperatures below 343 K⁽¹³⁾⁽¹⁴⁾. By using their thermodynamical data, we can calculate the a_{MOH} values under the conditions employed in the present study. The mean activity coefficient $\gamma_{\pm}$ of NaOH or KOH solution is given by eq. (5).

$$\log \gamma_{\pm} = \frac{u\sqrt{m}}{1+\sqrt{2}m} + Bm + Cm^2 + Dm^3 + Em^4, \quad (5)$$

where m is a molality of alkali and u is a constant determined by temperature and the type of solvent having a relation to Debye-Hückel limiting law. B , C , D and E are constants determined empirically.

The values of u for NaOH were given by Åkerlöf and Kegeles at temperatures below 343 K⁽¹³⁾, and those for KOH were reported by Åkerlöf and Bender⁽¹⁴⁾. Also the values of B , C , D and E were given in the same papers as a function of temperature. The values of u at higher temperatures than 343 K were determined by an extrapolation method. By using the calculated values of u and those of B , C , D and E , the values of a_{NaOH} and a_{KOH} were evaluated. Since no data were available for LiOH, the values of a_{LiOH} at 298 K⁽¹⁵⁾ were used instead of those at elevated temperatures.

In Fig. 5 apparent rate constants, which were shown in Fig. 4 at three different temperatures, were plotted against the values of a_{NaOH} . Although slight deviations were observed, the rate constants showed a linear relationship to a_{NaOH} at all temperatures studied.

A similar tendency was also observed for the oxidation reaction of As(III) in KOH solutions, as was illustrated in Fig. 6. This figure is a plot of k_1 determined for oxidation of As(III) at 383 K in aqueous solutions of three different alkalis. The values of a_{MOH} in NaOH and KOH were obtained at 383 K, while those in LiOH

Fig. 5 Effect of a_{NaOH} on reaction rates: $C_{\text{As(III)}} 5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$, $p_{\text{O}_2} 5.1 \times 10^5 \text{ Pa}$, Temp. 383 K, $\omega 16.7 \text{ s}^{-1}$.

solutions were obtained at 298 K. The values of a_{NaOH} as well as those of a_{KOH} increased by a factor of about 1.8 by elevation of the temperature from 298 to 383 K, and thus a similar tendency in a_{LiOH} change was expected by elevation of the temperature to 383 K.

A satisfactory linearity between k_1 and a_{MOH} can be observed in Fig. 6 for the oxidation reaction in NaOH and KOH solutions. But such a linearity was not obtained for LiOH. One of the reasons for such a deviation from a straight line observed for the LiOH system, might be inaccurate determination of oxidation rate due to white turbidity. This was probably caused by formation of lithium arsenate, which was detected in the solution as the reaction progressed. Therefore, we can write eq. (6) as the rate equation by taking the dependence on a_{MOH} into consideration.

$$R = k'_2 \cdot C_{\text{As(III)}} \cdot p_{\text{O}_2} \cdot a_{\text{MOH}} \quad (6)$$

By comparing oxidation rates of As(III) at 298 K in various alkaline solutions, in which no white precipitate was formed, the increasing tendency of the oxidation rate was noted according to the sequence of $\text{KOH} < \text{NaOH} < \text{LiOH}$. This order coincides with that of the degree of polarization of water molecule

Fig. 6 Effect of a_{MOH} on reaction rates for the oxidation of As(III) in various alkali solutions: $C_{\text{As(III)}} 5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$, $p_{\text{O}_2} 5.1 \times 10^5 \text{ Pa}$, Temp. 383 K, $\omega 16.7 \text{ s}^{-1}$. a_{LiOH} values used were those at 298 K.

hydrated to cations. Thus, the amount of free water available in these alkaline solutions decreased according to the sequence of $\text{KOH} > \text{NaOH} > \text{LiOH}$. The concentrations of As(III) which directly relate to the reaction in aqueous solutions ought to be changed with the amount of free water.

Apparent rate constants determined in NaOH solutions at different temperatures were displayed on an Arrhenius plot. The results are depicted in Fig. 7. The values of k'_2 in this figure were estimated from the slope, $\Delta k_1 / \Delta a_{\text{NaOH}}$, of straight line obtained by plotting k_1 against a_{NaOH} , as shown in Fig. 5. From Fig. 7, an apparent activation energy for the oxidation reaction of As(III) in NaOH solution was found to be $73.2 \text{ kJ} \cdot \text{mol}^{-1}$, which included the change in standard enthalpy of the dissolution of oxygen in aqueous NaOH solution.

No data are available on the solubilities of oxygen in aqueous NaOH solutions at temperatures from 343 to 383 K. A small change in standard enthalpy of oxygen dissolution is expected at this temperature range, because a temperature dependence of solubility of oxygen in pure water determined between 353 and 373 K is known to be small⁽¹⁶⁾. Further, standard enthalpy changes calculated

Fig. 7 Effect of temperature on reaction rates of the oxidation of As(III) in NaOH solutions: $C_{\text{As(III)}} 5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$, $p_{\text{O}_2} 5.1 \times 10^5 \text{ Pa}$, $\omega 16.7 \text{ s}^{-1}$.

from Henry constants of oxygen dissolution into pure water⁽¹⁷⁾ were found to be $-13 \text{ kJ} \cdot \text{mol}^{-1}$ at 298 K and less than $-1 \text{ kJ} \cdot \text{mol}^{-1}$ at 368 K. Therefore, the apparent activation energy mentioned above indicates that the oxidation reaction is controlled by a chemical reaction step. Actually no significant change in oxidation rates was detected by changing the agitation speed of solutions from 13.3 to 20.0 s^{-1} . This finding supports the mechanism of chemical reaction limitations.

As shown in Fig. 2, the oxidation reaction of As(III) in alkaline solution is suppressed by the resultant product As(V). A further examination was made on the effect of As(V) addition on the oxidation rate by changing NaOH concentrations at four levels. The results in Fig. 8 point to a larger effect of As(V) addition at higher NaOH concentrations when the oxidation rates were compared at the same temperature. For example, k_1 value determined in $4 \text{ kmol} \cdot \text{m}^{-3}$ NaOH solution containing $5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$ As(V) at 343 K was 37% lower than that determined without As(V) addition. The decrease in k_1 value in $3 \text{ kmol} \cdot \text{m}^{-3}$ NaOH was only 20%.

Figure 9 demonstrates the effect of a_{NaOH} on the apparent rate constant k_1 determined with or without the addition of As(V). The slopes of both straight lines were found to be unity,

Fig. 8 Effect of the addition of As(V) on reaction rates of the oxidation of As(III) in NaOH solutions: $C_{\text{As(III)}} 5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$, $p_{\text{O}_2} 5.1 \times 10^5 \text{ Pa}$, Temp. 343 K, $\omega 16.7 \text{ s}^{-1}$, C_{NaOH} : A $4 \text{ kmol} \cdot \text{m}^{-3}$, B $3 \text{ kmol} \cdot \text{m}^{-3}$, C $2 \text{ kmol} \cdot \text{m}^{-3}$, D $1 \text{ kmol} \cdot \text{m}^{-3}$.

Fig. 9 Effect of a_{NaOH} on reaction rates with or without the addition of As(V): $C_{\text{As(III)}} 5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$, $p_{\text{O}_2} 5.1 \times 10^5 \text{ Pa}$, Temp. 343 K, $\omega 16.7 \text{ s}^{-1}$, Initial $C_{\text{As(V)}}$ concentration: $\circ 0 \text{ kmol} \cdot \text{m}^{-3}$, $\bullet 5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$.

though the decrease in k_1 values was observed by adding $5 \times 10^{-2} \text{ kmol} \cdot \text{m}^{-3}$ As(V).

It is considered that the oxidation of As(III)

proceeds obeying the same mechanism, despite the presence of As(V) in the solution system, although the oxidation rate is slightly retarded by its presence.

On the other hand, the reduction sequence of dissolved molecular oxygen according to one electron transfer mechanism proceeds⁽¹⁸⁾ as follows:

Furthermore, we must consider the formation of As(IV), if this one electron transfer mechanism is applied to the present reaction system. In this regard, Wood *et al.* confirmed the existence of As(IV)⁽¹⁹⁾. It is also known that the chemical species of A(IV) is extremely unstable in an aqueous solution, and readily oxidized to As(V) with molecular oxygen⁽¹⁹⁾. Thus, As(IV) which is formed as an intermediate product, may be rapidly oxidized to As(V) with unstable reduced products of oxygen such as O_2^- and ${}^-\text{OOH}$.

The dependence of oxidation rate of As(III) in the presence of As(V) upon a_{NaOH} was found to be of the first order, and the concentration of reacting species is controlled by a_{NaOH} . NaOH, KOH and LiOH are strong electrolytes and may dissociate almost completely in aqueous solutions. Although it is necessary to elucidate the role of single ion activities instead of a_{MOH} in the oxidation reaction of As(III), no data on activities of single ions in the mentioned solution systems is available.

IV. Conclusion

The oxidation of As(III) with dissolved molecular oxygen in alkaline solutions was investigated kinetically. The oxidation rates of As(III) obey the equation,

$$R = k'_2 \cdot C_{\text{As(III)}} \cdot p_{\text{O}_2} \cdot a_{\text{MOH}},$$

at least in aqueous NaOH and KOH solutions. The major rate limiting step for the oxidation reaction appears to be a chemical reaction process. The evidences that support this analysis are an apparent activation energy of 73.2 kJ·mol⁻¹ and the reaction rates independent

of the agitation speed. The oxidation rates of As(III) increased in various alkaline solutions according to the sequence of KOH < NaOH < LiOH. This sequence coincides with the order of the amount of free water available in the solutions. It was also observed that the accumulation of As(V) tended to suppress the reaction slightly.

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