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The Kinetics of Oxygen Exchange between Arsenate Ions and Solvent Water

Akiko Okumura and Nobukazu Okazaki
Department of Chemistry, Nara Women's University, Nara 630

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The rates of oxygen exchange between arsenate ions and water have been measured at 14.5 °C and 30 °C over the pH range of 6.5—12.5. The rate, R, may be expressed by the rate law:

$$R = k_1[H_2AsO_4^-] + k_2[HAsO_4^{2-}] + k_3[AsO_4^{3-}] + k_4[H_2AsO_4^-]^2 + k_5[H_2AsO_4^-][HAsO_4^{2-}] + k_6[HAsO_4^{2-}]^2.$$

The exchange rates at 30 °C and $I=0.55$ have been analyzed in terms of this rate law to obtain the values of the rate constants, k_1—k_6. The activation energy of the over-all exchange reaction is 13.2±0.2 kcal/mol at pH 7.51 and 22.14±0.02 kcal/mol at pH 9.79. The reaction shows a negative salt effect in the region of pH 7.5, and a positive salt effect at pH 9.3.

The oxygen exchange of arsenate ions in an aqueous solution has been studied, except for the earlier qualitative studies,[1] mainly from the biochemical point of view.[2] In order to explore the possibility of the use of ^{18}O-labelled arsenate in biochemical tracer work, Kouba and Varner[3] have measured the exchange halftimes at several pH's between 2 and 10 at 32 °C; they estimated a very low activation energy of 3.7 kcal/mol for the exchange reaction at pH 8.0. We have studied the kinetics of this reaction in more detail in order to elucidate its mechanisms.

Experimental

Materials. Disodium hydrogen arsenate heptahydrate (Special grade, JIS) was recrystallized from water. Water enriched in oxygen-18 (*ca.* 2 atom%) and guanidine hydrochloride were treated as has been described in a previous paper.[4] Lithium perchlorate was obtained by neutralizing lithium carbonate (Special grade, JIS) with perchloric acid (Special grade, JIS), and was repeatedly recrystallized. The other chemicals were of an analytical reagent grade, and were used without further purification.

Procedure. The procedures were almost the same as those used in the previous work.[4] The exchange reaction was started by diluting an isotopically-equilibrated solution of disodium hydrogen arsenate in oxygen-18 water with a relatively large amount of isotopically normal water. The pH value of the solution was controlled by adding a small amount of hydrochloric acid or of a sodium hydroxide solution. The ionic strength was adjusted by the addition of sodium chloride. The reactions were carried out in an ice-water bath or in a constant temperature bath. At appropriate intervals a portion of the solution was removed, and the arsenate ions were precipitated by adding a barium chloride solution. The compositions of the precipitates from the solutions at pH 5.6 and 8.9 were shown by chemical analysis to be $BaHAsO_4 \cdot H_2O$. The precipitate was separated by means of a centrifuge, washed three times with absolute ethanol, dried in an oven at 110 °C, and converted into carbon dioxide by the guanidine hydrochloride method.[5] The isotopic analysis of the carbon dioxide was made on a Hitachi RMS-I-type mass spectrometer.

The rate of oxygen exchange in g atom per l in unit of time was calculated by means of the formulas:

$$R = \frac{4[\mathrm{As(V)}][H_2O]}{4[\mathrm{As(V)}]+[H_2O]} \cdot k_{\mathrm{ex}},$$

$$\text{and} \qquad k_{\mathrm{ex}} = -\frac{1}{t}\cdot \ln\left\{1-\frac{O_0-O_t}{O_0-O_\infty}\right\}, \qquad \text{(I)}$$

where O_0, O_t, and O_∞ are the oxygen-18 contents of the arsenate oxygen at the times 0, t, and infinity respectively, and where [As(V)] and $[H_2O]$ are the molar concentrations of the arsenate and water respectively. The McKay plots were satisfactorily linear over two half-lives except for the runs at pH>11.

Induced Exchange. It has been found in the preliminary work that oxygen exchange between arsenate ions and water is induced on the precipitation of arsenates by metallic ions. The extent of the induced exchange varies with the nature of the metallic ions; it is found to be larger for the ions of transition metals and for the cations with higher charges. With the barium ion as precipitant, which induces the oxygen exchange least of all the metal ions tried, the induced exchange amounts to *ca.* 20% of the total exchange at pH 9.0 and 30 °C. The extent increases with an increase in the acidity. Prestwood and Wahl[6] have discussed the effect of induced exchange on the kinetics of Tl(I)–Tl(III) exchange reaction. They have shown that, when the separation-induced exchange and the incomplete separation effects are reproducible, the equation of the form of (I), with the values of specific activities measured after separation, gives the real rate that occurs in solution. Their argument, with necessary changes, applies to the present case. The presence of the crystal water in the precipitate of barium arsenate may be treated as a case of incomplete separation in the sense of these authors. Since the precipitate has a definite composition, and since the oxygen-18 content of the crystal water is approximately equal to that of the normal water, we may make use of Eq. (I) in calculating the exchange rate in solution.

To check the above arguments experimentally, we have carried out the following two experiments. 1) In a kinetic run (pH 7.40, 30 °C), the precipitate of barium hydrogen arsenate monohydrate was divided into two portions. One portion was dried at 110 °C for an hour and then analysed as has been described above. Barium hydrogen arsenate monohydrate loses its water of crystallisation above 120 °C.[7]

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[1] T. Titani and K. Goto, This Bulletin, **14**, 77 (1939); N. F. Hall and O. R. Alexander, *J. Amer. Chem. Soc.*, **62**, 3455 (1940).

[2] D. H. Slocum and J. E. Varner, *J. Biol. Chem.*, **235**, 492 (1960); N. Itada and M. Cohn, *ibid.*, **238**, 2026 (1963).

[3] R. F. Kouba and J. E. Varner, *Biochem. Biophys. Res. Communs.*, **1**, 129 (1959).

[4] A. Okumura and N. Okazaki, This Bulletin, **46**, 1080 (1973).

[5] P. D. Boyer, D. J. Graves, C. H. Suelter, and M. E. Dempsey, *Anal. Chem.*, **33**, 1906 (1961).

[6] R. J. Prestwood and A. C. Wahl, *J. Amer. Chem. Soc.*, **71**, 3137 (1949).

[7] R. H. Vallance, "A Text-book of Inorganic Chemistry," ed. by J. N. Friends, Vol. VI, Part IV, (1938), Charles Griffin Co., London, p. 194.

The other portion was dehydrated at 170 °C for two hours to the anhydrous salt and then analysed for its oxygen-18 content. The two methods gave approximately equal ^{18}O-concentrations, the difference being not more than 5 per cent. This fact shows that the scrambling of oxygen atoms occurs between arsenate ions and crystal water in the course of the dehydration of barium hydrogen arsenate monohydrate. Similar phenomena have been observed with disodium hydrogen and sodium dihydrogen arsenates at room temperature.[8] The first-order rate constants of ^{18}O-exchange, k_{ex}, obtained by the two methods are 0.233 ± 0.001 hr^{-1} and 0.234 ± 0.002 hr^{-1} for the drying temperatures of 110 °C and 170 °C respectively. 2) An oxygen-exchange reaction of arsenate ions (pH 8.89, 30 °C, [As(V)]=1.2 M) was followed by two different methods of ^{18}O-analysis, one by analysing the arsenate oxygen by the method described above, and the other by measuring the increase in the ^{18}O-content of the solvent water. The solvent water was separated by the freeze-dry method and was analysed by the guanidine hydrochloride method. The values of k_{ex} obtained are 0.0880 ± 0.0002 hr^{-1} and 0.0928 ± 0.0007 hr^{-1} for the arsenate analysis and the water analysis respectively. Taking into consideration the difference in the analytical methods, the agreement between the two values of k_{ex} may be considered to be satisfactory. These results show that the induced exchange does not affect the kinetics of the oxygen-exchange reaction of arsenate ions.

Determination of the Dissociation Constants of Arsenic Acid. For the analysis of the exchange rate, it is desirable to obtain the pK_2 and pK_3 values of arsenic acid under the conditions of the kinetic runs. These have been determined by potentiometric titrations with a glass electrode. Solutions of potassium dihydrogen arsenate containing an amount of potassium chloride necessary to maintain the desired ionic strength were titrated with a solution of carbonate-free potassium hydroxide. The concentrations of the solutions were so chosen as to give the desired ionic strength at the half-neutralisation point. The values obtained are given in the following table.

TABLE 1. THE VALUES OF pK_2 AND pK_3 OF ARSENIC ACID[a)]

	Temp. °C	Ionic strength		
		0.13	0.30	0.55
pK_2	0	$6.83_7\pm0.00_5$	—	$6.59_6\pm0.01_5$
	14.5	$6.77_7\pm0.00_4$	—	$6.56_1\pm0.00_6$
	30.0	$6.75_0\pm0.00_3$	—	$6.53_1\pm0.01_4$
pK_3	14.5	—	$11.30_6\pm0.02_6$	$11.19_2\pm0.01_0$
	30.0	—	$11.21_5\pm0.01_3$	$11.01_5\pm0.01_0$

a) Here the dissociation constant is defined by $K=a_{H^+}\cdot[A^-]/[HA]$, where a_{H^+} is the activity of the hydrogen ion and where [HA] and [A$^-$] are the molar concentrations of an acid and its conjugate base. The values of the pK's were obtained from two series of titrations, each with ten titrations. The errors indicated are the probable errors.

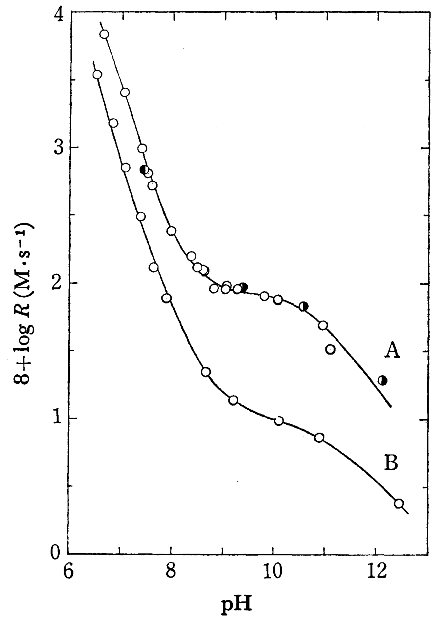

Fig. 1. pH-Rate profiles of the oxygen exchange between arsenate ions and water at 30°(A) and 14.5 °C(B). I=0.55 M (○: NaCl, ◐: NaClO$_4$, ◑: LiClO$_4$). [As(V)] $\simeq 6.8\times10^{-2}$ M. The curves at 30 °C were calculated by the use of the rate constants obtained.

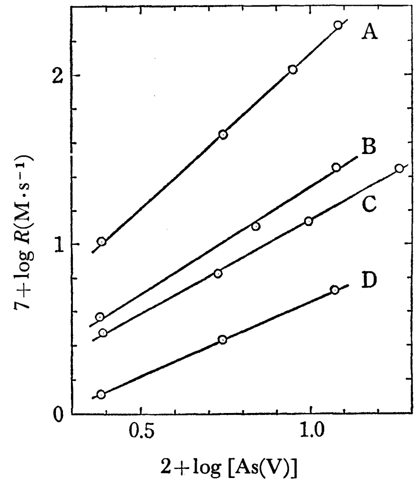

Fig. 2. Dependence of the exchange rate on [As(V)]. 30 °C. I=0.55 M. A: pH 7.51, B: pH 8.47, C: pH 9.27, D: pH 11.1.

Results and Discussion

pH *Dependence of the Exchange Rate.* The dependence of the exchange rate on the pH is shown in Fig. 1. In the neighbourhood of pH=pK_2, the logarithm of the rate varies linearly with the pH, and the rate is approximately first-order in the hydrogen-ion concentration. At pH$\simeq$9, the dissociation of H$_2$AsO$_4^-$ is almost complete and the dissociation of HAsO$_4^{2-}$ begins. In this pH region, the variation in the exchange rate with the pH slows down, and at 30 °C the rate is nearly independent of the pH. At pH>10, the rate falls off again with the increase in the dissociation of HAsO$_4^{2-}$.

Dependence on the Total Arsenate Concentration, [As(V)]. This was studied at four pH's, 7.51, 8.47, 9.27, and 11.1, at 30 °C and I=0.55 M (Fig. 2). Plots of log R against log [As(V)] yield straight lines with slopes of 1.83 ± 0.02, 1.26 ± 0.03, 1.11 ± 0.01, and 0.89 ± 0.01 for the pH values of 7.51, 8.47, 9.27, and 11.1 respectively.

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8) A. Okumura and N. Okazaki, This Bulletin, **46**, 2981 (1973).

Mechanisms of the Oxygen Exchange. At pH$\simeq$7.5 and at 30 °C, the rate of oxygen exchange may be expressed as $R=k[H^+][As(V)]^{1.8}$. In this region, bimolecular mechanisms between arsenate ions predominate:

$$H_2AsO_4^- + H_2AsO_4^- \overset{k_4}{\rightleftharpoons} H_2As_2O_7^{2-} + H_2O, \qquad (4)$$

$$H_2AsO_4^- + HAsO_4^{2-} \overset{k_5}{\rightleftharpoons} HAs_2O_7^{3-} + H_2O, \qquad (5)$$

$$HAsO_4^{2-} + HAsO_4^{2-} \overset{k_6}{\rightleftharpoons} As_2O_7^{4-} + H_2O. \qquad (6)$$

The role of the hydrogen ion is to shift the pre-equilibrium:

$$H_2AsO_4^- \rightleftharpoons HAsO_4^{2-} + H^+,$$

from right to left in favour of the more reactive arsenate species, $H_2AsO_4^-$. It has been believed that the diarsenate ion hydrolyzes very rapidly and therefore cannot exist in aqueous solutions.[9] However, the present result shows that, in an aqueous solution, the condensation of the arsenate ions occurs as well as the hydrolysis of the diarsenate ion. The order with respect to the [As(V)] of 1.8 suggests the occurrence of some first-order paths of the oxygen exchange. These are probably:

$$H_2AsO_3O^{*-} + H_2O \overset{k_1}{\rightleftharpoons} H_2AsO_4^- + H_2O^*, \qquad (1)$$

and

$$HAsO_3O^{*2-} + H_2O \overset{k_2}{\rightleftharpoons} HAsO_4^{2-} + H_2O^*\cdot \qquad (2)$$

In the region of pH$\simeq$9 at 30 °C, where the dissociation of $H_2AsO_4^-$ is almost complete and where $HAsO_4^{2-}$ begins to dissociate, the observed rate law is $R\simeq k'[H^+]^0[As(V)]^{1.1}$. Since, in this region, $[HAsO_4^-]$ is nearly independent of pH, a zero-order dependence on $[H^+]$ may be expected. The observed [As(V)] dependence of 1.1 suggests that, above pH 9, the first-order path (2) controls the total exchange rate. At pH 11.1, the contribution of the bimolecular path (6) becomes negligible. In addition to the above five paths, a pseudo-first-order path:

$$AsO_3O^{*3-} + H_2O \overset{k_3}{\rightleftharpoons} AsO_4^{3-} + H_2O^*, \qquad (3)$$

may be expected to make a contribution, if slight, to the total rate.

The rate law of oxygen exchange of arsenate ions may be written as:

$$\begin{aligned} R &= R_1 + R_2 + R_3 + R_4 + R_5 + R_6 \\ &= k_1[H_2AsO_4^-] + k_2[HAsO_4^{2-}] + k_3[AsO_4^{3-}] \\ &\quad + k_4[H_2AsO_4^-]^2 + k_5[H_2AsO_4^-][HAsO_4^{2-}] \\ &\quad + k_6[HAsO_4^{2-}]^2. \end{aligned} \qquad (7)$$

Temperature Dependence of the Exchange Rate. This has been studied at pH 7.51 (0 °C, 20 °C, and 30 °C) and at pH 9.79 (30 °C, 40 °C, and 50 °C). Plots of log R against $1/T$ are shown in Fig. 3. From the slopes of the plots, the values of the activation energy are calculated to be 13.2±0.2 kcal/mol at pH 7.51 and 22.14±0.02 kcal/mol at pH 9.79. At 30 °C and pH 9.79, it can be estimated that nearly 95% of the oxygen exchange occurs through Path (2). The value of 22 kcal/mol gives the approximate value of the activation energy of this path. At 30 °C and pH 7.51, the contributions of the second-order rate terms, R_4 and R_5, to the total rate are estimated to be 44 and 38% respectively. The value of 13 kcal/mol gives an upper limit for the activation energies of these bimolecular paths between arsenate ions.

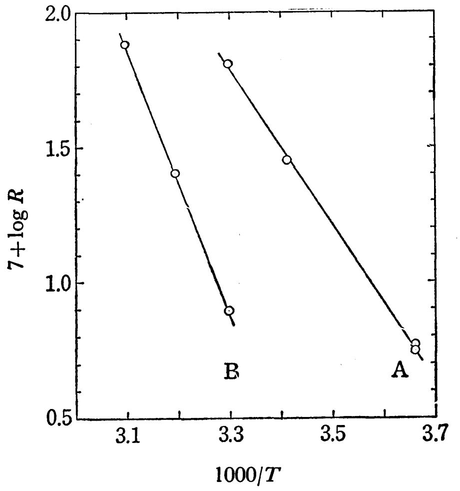

Fig. 3. Temperature dependence of the exchange rate at pH 7.51(A) and 9.79(B). [As(V)]=0.068 M, I=0.55 M.

Salt Effect. On the rate-pH profile at 30 °C (Fig. 1), the plots at pH 7.45, 9.37, 10.58, and 12.12 were obtained with solutions whose ionic strengths had been adjusted with sodium or lithium perchlorate instead of sodium chloride. These plots fall on a curve with the other plots within the range of experimental error. This fact shows the absence of any specific effects of the chloride and perchlorate ions.

The effect of the ionic strength on the exchange rate has been studied at 30 °C at pH 7.72 and 9.29. At a fixed total concentration of the arsenate, the ionic strength was varied by the addition of sodium chloride. The values of the exchange rate thus obtained are listed in the following table:

Table 2. The effect of the ionic strength on the exchange rate ($R\times10^6$) at 30°C

pH	Ionic strengths.			
	0.2	0.55	0.7	1.0
7.72	5.64	—	5.07	3.83
9.29	0.854	0.906	—	0.926

The salt effect is negative at pH 7.72 and positive at pH 9.29. The exchange paths (4), (5), and (6), which predominate in the region of pH 7.72 are expected to exhibit a positive salt effect. Thus, the negative salt effect observed must be due to an equilibrium salt effect which overcomes the kinetic salt effect. An increase in the ionic strength decreases the concentration of the more active species, $H_2AsO_4^-$, by increasing the dissociation constant of $H_2AsO_4^-$. In the region of pH 9, where the extent of the dissociation of

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[9] "Gmelins Handbuch der Anorganischen Chemie," 8-te Aufl. Syst. -Nr. 17, (1952), Verlag Chemie, Weinheim/Bergstrasse. S. 358.

$HAsO_4^{2-}$ is small, the change in the dissociation constant of $HAsO_4^{2-}$ is without appreciable effect on the concentration of $HAsO_4^{2-}$, and so the kinetic salt effect predominates.

Analysis of the Exchange Rate at 30 *°C.* The exchange rates observed can be analyzed by the use of the rate law (7). The concentrations of the ionic species were calculated by the relations:

$$[\mathrm{As(V)}] = [\mathrm{H_2AsO_4^-}] + [\mathrm{HAsO_4^{2-}}] + [\mathrm{AsO_4^{3-}}], \tag{8}$$

$$K_2 = a_{\mathrm{H^+}}\cdot[\mathrm{HAsO_4^{2-}}]/[\mathrm{H_2AsO_4^-}], \tag{9}$$

$$K_3 = a_{\mathrm{H^+}}\cdot[\mathrm{AsO_4^{3-}}]/[\mathrm{HAsO_4^{2-}}]. \tag{10}$$

Over the range of pH<9, the k_3-term in the rate law may be neglected, and by using the (8), (9), and (10) relations, Eq. (7) can be rewritten in the form:

$$\frac{R}{[\mathrm{H_2AsO_4^-}]} = \left(k_1 + k_2\frac{K_2}{a_{\mathrm{H^+}}}\right) + [\mathrm{As(V)}] \times \left\{\frac{k_4}{1+(K_2/a_{\mathrm{H^+}})+(K_2K_3/a_{\mathrm{H^+}}^2)} + \frac{k_5}{1+(a_{\mathrm{H^+}}/K_2)+(K_3/a_{\mathrm{H^+}})} + \frac{k_6}{(a_{\mathrm{H^+}}/K_2)\{1+(a_{\mathrm{H^+}}/K_2)+(K_3/a_{\mathrm{H^+}})\}}\right\}. \tag{11}$$

In Fig. 4, the data of Fig. 2 are replotted according to Eq. (11). The least-squares treatment of the plots yields:

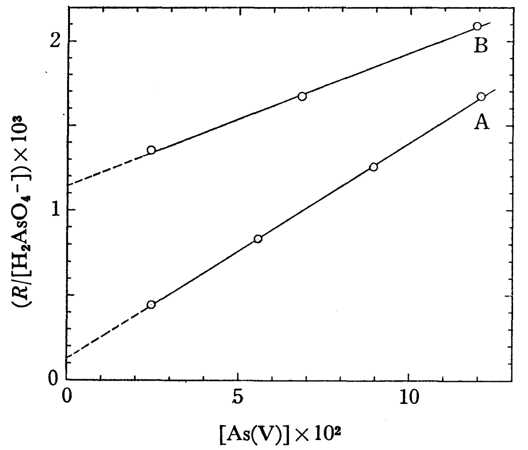

Fig. 4. $R/[\mathrm{H_2AsO_4^-}]$ as a function of [As(V)] at pH 7.51(A) and 8.47(B) at 30 °C.

$$k_1 + 9.48k_2 = (0.124 \pm 0.006) \times 10^{-3}, \tag{12}$$

$$0.954k_4 + 0.905k_5 + 8.58k_6 = (0.128\pm0.001)\times10^{-1}, \text{ at pH 7.51}, \tag{13}$$

and:

$$k_1 + 87.7k_2 = (1.15\pm0.02) \times 10^{-3}, \tag{14}$$

$$0.0112k_4 + 0.986k_5 + 86.5k_6 = (0.0784\pm0.002)\times10^{-1}, \text{ at pH 8.48}. \tag{15}$$

In the region of pH>9, by neglecting the k_1- and k_4-terms, Eq. (7) can be transformed into:

$$\frac{R}{[\mathrm{HAsO_4^{2-}}]} = \left(k_2 + k_3\frac{K_3}{a_{\mathrm{H^+}}}\right) + [\mathrm{As(V)}]\left\{\frac{k_5}{1+(K_2/a_{\mathrm{H^+}})+(K_2K_3/a_{\mathrm{H^+}}^2)} + \frac{k_6}{1+(a_{\mathrm{H^+}}/K_2)+(K_3/a_{\mathrm{H^+}})}\right\}. \tag{16}$$

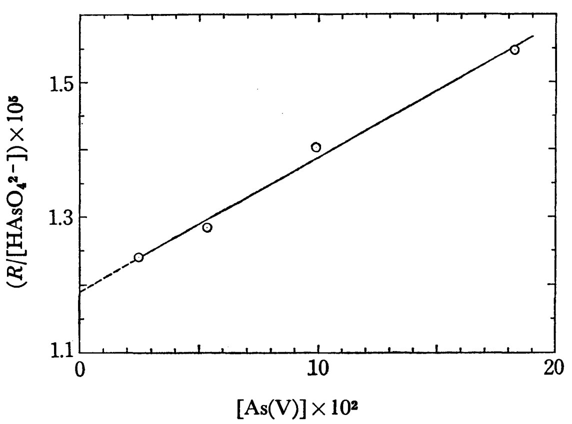

Fig. 5. $R/[\mathrm{HAsO_4^{2-}}]$ as a function of [As(V)] at pH 9.27 and 30 °C.

Fig. 5 shows a plot of $R/[\mathrm{HAsO_4^{2-}}]$ against [As(V)] at pH 9.27 and I=0.55 M, the data used being the same as those of Fig. 2C. From the intercept and the slope of a line passing through the plots, we obtain:

$$k_2 + 0.0179k_3 = (1.19\pm0.01) \times 10^{-5}, \tag{17}$$

and

$$0.00180k_5 + 0.981k_6 = (0.0198\pm0.0008) \times 10^{-3}. \tag{18}$$

Since k_2 may be reasonably assumed to be larger than k_3, the value of k_2 may be fixed from (17), with an uncertainty of 2% at most to be:

$$k_2 = (1.19\pm0.01) \times 10^{-5}\,\mathrm{s^{-1}}.$$

Eqs. (13), (15), and (18) can be solved simultaneously for k_4, k_5, and k_6. The results are:

$$k_4 = 0.74 \times 10^{-1}\,\mathrm{M^{-1}s^{-1}},$$

$$k_5 = 0.64 \times 10^{-2}\,\mathrm{M^{-1}s^{-1}},$$

and $k_6 = 0.85 \times 10^{-5}\,\mathrm{M^{-1}s^{-1}}$.

The value of k_1 is subject to some uncertainty. By using the value of k_2 obtained above, k_1 is evaluated from (12) to be 1.1×10^{-4} and from (14) to be 1.1×10^{-5}. The former value may be better, because the k_1-path plays a more important role at pH 7.51 than at pH 8.48.

The value of k_3 is also attended with uncertainty, because the k_3-path plays an important role only in the most alkaline region of this study, where experimental troubles make the exact determination of the exchange rate difficult. At pH>9.5, where the contribution of the k_5-path to the total rate is negligible, the rate law (7) becomes:

$$R = k_2[\mathrm{HAsO_4^{2-}}] + k_3[\mathrm{AsO_4^{3-}}] + k_6[\mathrm{HAsO_4^{2-}}]^2,$$

which can be transformed into:

$$R - k_6[\mathrm{HAsO_4^{2-}}]^2 = k_2[\mathrm{As(V)}] + (k_3-k_2)[\mathrm{AsO_4^{3-}}].$$

In this pH region, the contribution of the k_6-term is small, being *ca.* 5% of the total rate at pH 9.79. Fig. 6 shows a plot of $R-k_6[\mathrm{HAsO_4^{2-}}]^2$ against $[\mathrm{AsO_4^{3-}}]$ at a constant value of [As(V)], the value of k_6 obtained above being used. The observed rates were normalized to $[\mathrm{As(V)}]=6.8\times10^{-2}$ M by assuming $R\propto[\mathrm{As(V)}]$. The least-squares treatment of the plots yields the value: $k_2[\mathrm{As(V)}]=(0.080\pm0.003)\times10^{-5}$, and $k_3-k_2=-(0.010\pm0.001)\times10^{-3}$, whence we ob-

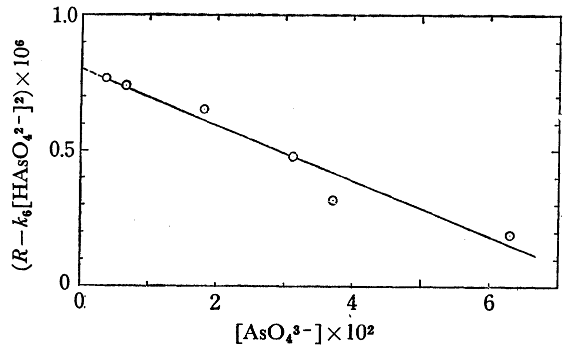

Fig. 6. A plot of $R-k_6[HAsO_4^{2-}]^2$ against $[AsO_4^{3-}]$. 30 °C. $[As(V)]=0.068$ M. $I=0.55$ M.

tain:

$$k_2 = 1.18\times10^{-5}\,s^{-1},$$

and

$$k_3 = 0.15\times10^{-5}\,s^{-1}.$$

The values of the rate constants obtained are summarized in the following table. Other methods of evaluating the rate constants yielded values which are in satisfactory agreement with those above. The rate-pH profile at 30 °C in Fig. 1 was calculated by using these rate constants; it shows a satisfactory agreement with the plots obtained by the experiments except for the most alkaline region.

The rate constant, k_1', of the oxygen exchange of dihydrogen phosphate ions:

$$H_2PO_4^- + H_2O^* \rightleftharpoons H_2PO_3O^{*-} + H_2O,$$

has been found to be $4\times10^{-6}\,s^{-1}$ at 100 °C.[10] If the activation energy of this process is assumed to be about the same as that of the hydrolysis of the monoanion of methyl dihydrogen phosphate (30 kcal/mol),[10] k_1' has a value of 4×10^{-10} at 30 °C, which is smaller by a factor of 10^6 than the corresponding rate constant, k_1, of the dihydrogen arsenate ion.

TABLE 3. RATE CONSTANTS OF THE OXYGEN EXCHANGE BETWEEN ARSENATE IONS AND WATER AT 30 °C (I=0.55 M)

Exchange path	Rate constants
$H_2AsO_4^- + H_2O \rightleftharpoons$	k_1: $1\times10^{-4}\,s^{-1}$
$HAsO_4^{2-} + H_2O \rightleftharpoons$	k_2: $1.2\times10^{-5}\,s^{-1}$
$AsO_4^{3-} + H_2O \rightleftharpoons$	k_3: $1.5\times10^{-6}\,s^{-1}$
$H_2AsO_4^- + H_2AsO_4^- \rightleftharpoons H_2As_2O_7^{2-} + H_2O$	k_4: $7.4\times10^{-2}\,M^{-1}s^{-1}$
$H_2AsO_4^- + HAsO_4^{2-} \rightleftharpoons HAs_2O_7^{3-} + H_2O$	k_5: $6.4\times10^{-3}\,M^{-1}s^{-1}$
$HAsO_4^{2-} + HAsO_4^{2-} \rightleftharpoons As_2O_7^{4-} + H_2O$	k_6: $8.5\times10^{-6}\,M^{-1}s^{-1}$

A hydrogen-bonded cyclic intermediate between a dihydrogen phosphate ion and a water molecule has been postulated for the oxygen exchange of dihydrogen phosphate ions.[11] Such a special reactivity of the monoanion was not observed in the oxygen exchange of arsenate ions, the rate constant, k_1, being only an order of magnitude larger than k_2, which in turn is also an order of magnitude larger than k_3. The exchange paths, (1)—(3), involve probably the nucleophilic attack of a water molecule on the arsenic atom of arsenate ions.

From the values of the constant, k_2, and the activation energy of Path (2) (22 kcal/mol), the entropy of activation of this path is calculated to be $\Delta S^{\neq}_2=-11$ cal K^{-1} mol^{-1} (30 °C). This value is consistent with a mechanism which involves a bimolecular substitution process between an arsenate ion and a water molecule as the rate-limiting step.

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[10] C. A. Bunton, D. R. Llewellyn, K. G. Oldham, and C. A. Vernon, *J. Chem. Soc.*, **1958**, 3574.

[11] C. A. Bunton, D. R. Llewellyn, C. A. Vernon, and V. A. Welch, *ibid.*, **1961**, 1636.