Algorithm for Computer-Aided Construction of the Potential-pH Diagrams of Metal-Ion-Water Systems and Its Application to the Corrosion in Iodine-Iodide Solution*

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An algorithm to construct the potential-pH diagram of metal-ion-water systems by using a computer was established and it is applied to the metal-iodine-water system to explain the corrosion behavior of metals in the environment corresponding to the first stage reaction of the Magnesium-Iodine Cycle of thermochemical hydrogen production process. It is concluded that Ta, Zr, and Ti are thermodynamically protected owing to the oxide films which are more stable than iodides considered. On the contrary, noble metals such as Au, Ag, and Pt are predicted to corrode in concentrated iodine-iodide solution. Thermodynamic prediction is in fairly good agreement with the experimental results reported before.

Key words: corrosion, iodine, iodide, computer, potential-pH diagram, hydrogen production

1. Introduction

In realizing thermochemical hydrogen production from water, material selection and/or development for the equipments is one of the most important problems. The Magnesium-Iodine Cycle, which was proposed by the National Chemical Laboratory for Industry, Japan, is no exception. It is composed of four reactions as follows:

- \[ \frac{6}{5}\text{MgO} + \frac{6}{5}\text{I}_2 \rightarrow \text{MgI}_2 + \frac{1}{5}\text{Mg(IO}_3\text{)}_2 \]
- \[ \frac{1}{5}\text{Mg(IO}_3\text{)}_2 \rightarrow \frac{1}{5}\text{MgO} + \frac{1}{5}\text{I}_2 + \frac{1}{2}\text{O}_2 \]
- \[ \text{MgI}_2 + \text{H}_2\text{O} \rightarrow \text{MgO} + 2\text{HI} \]
- \[ 2\text{HI} \rightarrow \text{H}_2 + \text{I}_2 \]

Among the four reactions, only the first stage reaction proceeds in aqueous solution. The corrosion behavior of metallic materials in this environment was already studied and it is concluded that (1) Ta and Nb are perfectly protective, (2) Zr is protective under a limited condition, (3) Some Ti alloys (Ti-5Ta, Ti-10Mo) and Hastelloy-C are sometimes protective but sometimes non-protective, and (4) noble metals such as Ag and Au corrode very rapidly.

These corrosion behaviors may be explained from thermodynamic point of view, but the potential-pH (E-pH) diagrams, the most effective means of describing the thermodynamic relations of metal-iodine-water systems, have not been reported yet.

Although principles of the E-pH diagram have been well-established, its construction is somewhat a cumbersome task, especially in the case where elements other than hydrogen, oxygen, and metal coexist because of the necessity of numerous calculations of Nernst’s equation etc. and solution of sets of algebraic equations. The use of computer in the construction of the E-pH diagram was first proposed by Brook and was followed by several researchers for metal-water system. As for the metal-iodine-water system, the algorithm proposed by Froning et al. is the only method that has a rigid base among algorithms categorized as a continuum type analysis (not the ‘point by point’ analysis), and it has been extensively applied by Chen et al.

The purpose of the present paper is (1) to establish an improved algorithm for the construction of the E-pH diagram of metal-ion-water systems, and (2) to apply it to the metal-iodine-water systems so as to explain the corrosion behavior of metals in concentrated iodine solution.

2. Algorithm for the Construction of E-pH Diagram

For convenience sake, the algorithm is explained separately in the following two cases: (1) ‘simple’ system where the chemical species contain only one element other than oxygen and/or hydrogen

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* Presented at Annual Meeting of Japan Society of Corrosion Engineering in May, 1986 (Tokyo).
(Study on Construction Materials for the Magnesium-Iodine Cycle of Thermochemical Hydrogen Production Process, Part 8)

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(species of the type of \{\text{Me}m_1\text{O}x_1\text{Hy}z_1^{\pm}\} or \{\text{W}w_2\text{O}x_2\text{Hy}z_2^{\pm}\}), and (2) 'complex' system where the chemical species contain the second element (species of the type of \{\text{Me}m_3\text{W}w_3\text{O}x_3\text{Hy}z_3^{\pm}\}).

In the notation above and below, 'Me' denotes the metal to be considered and 'W', the second element such as iodine, while 'O' indicates oxygen. 'H', 'H^+' and 'el-' indicate hydrogen, hydrogen ion, and an electron, respectively.

### 2.1 Simple systems

The method used here in the construction of the E-pH diagram of a simple system is the same as that proposed by Froning et al.\(^3\), which is shown in Fig. 1 and described below. (Convex Polygon Method)

First, among all species to be considered, the 'area of predominance' (a.p.) of a species is determined in the E-pH diagram where it is more stable thermodynamically than any other species, by considering the reactions with all other species. For instance, the equilibrium of \{\text{Me}m_1\text{O}x_1\text{Hy}z_1^{\pm}\} with \{\text{Me}m_2\text{O}x_2\text{Hy}z_2^{\pm}\} determines the limit of a.p. of the former substance because of the reaction,

\[
\text{[Me}_{m_1}\text{O}_{x_1}\text{H}_{y_1}^{z_1^{\pm}}]\text{+Me}\text{=Me}_{m_2}\text{O}_{x_2}\text{H}_{y_2}^{z_2^{\pm}}\text{+Ca}[\text{H}_2\text{O}],
\]

where

\[
M=(m_2/m_1)(y_2-2x_2)+(2x_1-y_2),
\]

\[
Z=[z_1-(m_1/m_2)x_2]\text{+}(m_1/m_2)(y_2-2x_2)+(2x_1-y_1),
\]

\[
B=m_1/m_2, \quad C=x_1-(m_1/m_2)x_2.
\]

The chemical species \{\text{Me}m_1\text{O}x_1\text{H}_{y_1}^{z_1^{\pm}}\} is more stable than \{\text{Me}m_2\text{O}x_2\text{H}_{y_2}^{z_2^{\pm}}\} in the region where the following inequality is satisfied

\[
E>E^0-(RT/ZF)\text{log}\left(\text{ai}/\text{a}_2\right)B+(RT/ZF)2.303\text{pH}
\]

if \(Z>0\). \(E^0\) is the standard electrode potential of the redox system at T. By considering all of this kind of inequalities which represent the equilibria with other species (\{\text{Me}m_3\text{W}w_3\text{O}x_3\text{Hy}z_3^{\pm}\}), the a.p. of \{\text{Me}m_1\text{O}x_1\text{H}_{y_1}^{z_1^{\pm}}\} is determined as the area where all the inequalities are satisfied simultaneously.

Secondly, each a.p. of the species considered is compiled, resulting in the E-pH diagram of Me-H\(_2\)O. The same procedure is valid in the construction of the E-pH diagram of W-H\(_2\)O system.

### 2.2 Area of Predominance of Complex Systems

For the Me-W-H\(_2\)O system in which element W has its own E-pH equilibria (e.g. HI, I\(^-\), and I\(_2\)), the E-pH diagram cannot be determined by the Convex Polygon Method described above directly, since the a.p. does not always constitute a convex polygon\(^{*2}\). Froning et al.\(^9\) and Chen et al.\(^8\) used the following procedure: (1) to determine the a.p. of the species of the second element, W (e.g., HI, I\(^-\), I\(_2\), ...), (2) to determine the additional diagrams (one for each of the second element species) for the redox system containing the first element (Me) and each second element species, individually, and (3) to construct the final diagram by using the appropriate portion of each of the additional diagrams, by taking into account the a.p. of each of second species.

\(^{*1}\) When \(Z<0\), the direction of inequality sign is reverse. When \(Z=0\), the boundary line of the area of predominance is vertical on the E-pH diagram.

\(^{*2}\) There are cases where the a.p. of Me-W-O-H compound (\{\text{Me}m_3\text{W}w_3\text{O}x_3\text{Hy}z_3^{\pm}\}) has an interior angle larger than \(\pi\) radian at the boundaries of the a.p.'s on the E-pH diagrams of Me-H\(_2\)O and W-H\(_2\)O, as is shown in the example of Fe-S-H\(_2\)O system\(^{17}\).
The above procedure is rigorously correct in resolving equilibria between the first element species and the second element species, and therefore, never fails to construct a diagram. However, this algorithm executes unnecessary computation in the construction of additional diagrams in step (2), resulting in consumption of computer time and memory area than minimum requirement. This disadvantage seems to be serious when chemical species contain the third (or fourth, etc.) element that has its own E-pH equilibria (e.g. the case where FeI2.2NH3 is formed).

The algorithm proposed in this paper for determination of the a.p. of the Me-W-O-H compound \(\{\text{Me}_3\text{W}_3\text{O}_{3z}\text{H}_{2y}\}^{z+}\) within the area limited in step (1), by considering the reaction with \(\{\text{Me}_3\text{O}_2\text{H}_1\}^{z+}\), \(\{\text{Me}_4\text{W}_2\text{O}_{4z}\text{H}_{4y}\}^{z+}\), \(\{\text{Me}_5\text{W}_5\text{O}_{5z}\text{H}_{5y}\}^{z+}\), \(\ldots\), and \(\{\text{W}_2\text{O}_{2z}\text{H}_{2y}\}^{z+}\), and (3) to conduct the step (1) and (2) for all the possible pairs of Me-O-H compounds and W-O-H compounds, resulting in the determination of a.p. of \(\{\text{Me}_3\text{W}_3\text{O}_{3z}\text{H}_{2y}\}^{z+}\) on the whole region of the E-pH diagram.

The procedure for the determination of the common area of two a.p.'s (step (1)) is as follows: (1-a) to check if the vertices, which determine the a.p. of \(\{\text{Me}_1\text{O}_1\text{H}_1\}^{z+}\) are the inner point of the a.p. of \(\{\text{W}_2\text{O}_{2z}\text{H}_{2y}\}^{z+}\) or not (If so, those points are the candidates of the vertices of the common area.), (1-b) to check if the vertices, which determine the a.p. of \(\{\text{W}_2\text{O}_{2z}\text{H}_{2y}\}^{z+}\) are the inner point of the a.p. of \(\{\text{Me}_1\text{O}_1\text{H}_1\}^{z+}\) or not (If so, those points are also the candidates of the vertices of the common area.), (1-c) to check if the sides of the a.p. of \(\{\text{Me}_1\text{O}_1\text{H}_1\}^{z+}\) intersect with those of the a.p. of \(\{\text{W}_2\text{O}_{2z}\text{H}_{2y}\}^{z+}\) (If so, the points of intersection are the candidates of the vertices of the common area.), and (1-d) to arrange the order of the candidates, which were determined in steps (1-a)~(1-c), to make a convex polygon.

In the steps (1-a) and (1-b), the so-called 'polygon test' in computer graphics\(^3\) is used; that is, if a point is inner point in the polygon, then the sum of the interior angles around that point is \(2\pi\) radian, and vice versa.

(b) Principle of maximum interior angle: The interior angle around a certain vertex has the biggest value when the candidates of the adjacent (fore- and hind-) vertices of that vertex is chosen rightly in a convex polygon. This principle is applied in order to arrange the candidate vertices in proper order.

The balancing equation used in step(2) for the reaction of \(\{\text{Me}_3\text{W}_3\text{O}_{3z}\text{H}_{2y}\}^{z+}\) and \(\{\text{Me}_4\text{W}_2\text{O}_{4z}\text{H}_{4y}\}^{z+}\) (when \(w_4=0\), the latter also represents the Me-O-H compound) is as follows:

\[
[M_{3m}\text{W}_3\text{O}_{3z}\text{H}_{2y}^{z+}] + M*[H^+] + A*[W_2\text{O}_{2z}\text{H}_{2y}^{z+}] + Z*[el^-] = B*[M_{4m}\text{W}_2\text{O}_{4z}\text{H}_{4y}^{z+}] + C*[H_2O],
\]

where

\[
M = -y_3-(y_2/w_2)*(m_3*w_4/m_4-w_3) + 2*s_3+2*s_2*(m_3*w_4/m_4-w_3)/w_2 - 2*m_3*s_4/m_4 + m_3*s_4/m_4,
\]

\[
A = (m_3*w_4/m_4-w_3)/w_2,
\]

\[
Z = z_3 + z_2*[m_3*w_4/m_4-w_3]/w_2 - m_3*s_4/m_4 - y_3 - y_2*[m_3*w_4/m_4 - w_3]/w_2 + 2*s_3 + 2*s_2*[m_3*w_4/m_4 - w_3]/w_2 - 2*m_3*s_4/m_4 + m_3*s_4/m_4,
\]

\[
B = m_3/m_4,
\]

\[^3\)\] Note that the a.p. of Me-W-O-H compound is convex if we consider it on the common area of the a.p.'s of \(\{\text{Me}_3\text{O}_2\text{H}_1\}^{z+}\) and \(\{\text{W}_2\text{O}_{2z}\text{H}_{2y}\}^{z+}\), though the a.p. of Me-W-O-H compound on the whole region of the E-pH diagram is not always convex.

\[^4\)\] This algorithm is valid because the common area of two convex polygon is also convex.
C = x_1 + x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8 + x_9 + x_{10}.

\{Me_{m1}W_{w1}O_{x1}H_{y1}^{z1+}\} is more stable than \{Me_{m2}W_{w2}O_{x2}H_{y2}^{z2+}\} in the region which satisfy the following inequality

\[ E > E^* - (RT/ZF)\log M + 2.303 \times pH \]

if \( Z > 0 \)

The reactions of FeI_2 with Fe_3O_4, FeI^+, or FeI^- on the common area of a.p.'s of Fe_3O_4 on Fe-H_2O system and I^- on I-H_2O system are as follows:

FeI_2 + (8/3)*H^+ + (2)*I^- + (2)*e^- = (1/3)*Fe_3O_4 + (4)*H_2O,

FeI_2 + (1)*I^- + (1)*e^- = FeI^+,

FeI_2 + (1)*I^- + (1)*e^- = FeI^-.

FeI_2 is stable in the area where the following inequalities, which correspond to the above reactions, are simultaneously satisfied.

\[ E < 1.5873 - 0.2367 \times pH, \]

\[ E < 0.716, E < 0.710. \]

The algorithm developed here is easily expanded into the cases where chemical species contain more than two elements besides oxygen, hydrogen, and metal.

### 3. On the Thermodynamic Data

Values of Gibbs energy and related quantities (e.g., stability constants of coordination compounds) to calculate the equilibria exist sporadical-
<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>SUBSTANCES (state*)</th>
<th>ADOPTED DATA (ref.*)</th>
<th>OTHER DATA (ref.*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H₂(g): 0.0, H₂O(l): -56.7 (P, N, B)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>Ag⁺(aq): -22.0(N), Ag⁺(aq): 6.6(N), Ag²⁺(aq): -2.68(N), Ag³⁺(aq): -2.59(P), Ag⁺(aq): 29.0(N), Ag⁺(aq): -5.5(P), Ag⁺(aq): 18.4(N), Ag⁺(aq): 64.1(N), Ag⁺(aq): -62.2(N), Ag⁺(aq): -15.8(N), Ag⁺(aq): -15.7(S), Ag⁺(aq): -2.9(N), Ag⁺(aq): -22.4(N), Ag⁺(aq): -20.8(N), Ag⁺(aq): -21.2(C), Ag⁺(aq): -36.8(N), Ag⁺(aq): -37.8(C), Ag⁺(aq): -50.1(N), Ag⁺(aq): -50.5(C)</td>
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<tr>
<td>Au</td>
<td>Au⁺(aq): -75.8(L), Au⁺(aq): -67.8(L), Au⁺(aq): 42.0(L), Au⁺(aq): 105.2(L), Au⁺(aq): -12.4(L), H₂AuO₃⁻(aq): -33.9(L), H₂AuO₄⁻(aq): -52.1(L), Au⁺(aq): -0.12(L), Au⁺(aq): -11.4(L), Au⁺(aq): -10.8(L)</td>
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<td></td>
</tr>
<tr>
<td>Cr</td>
<td>Cr⁺(aq): -140.5(P), Cr⁺(aq): -215.3(P), Cr⁺(aq): -242.4(P), Cr⁺(aq): -250.2(P), Cr⁺(aq): -126.3(B), Cr⁺(aq): -626.6(B), Cr⁺(aq): -120.0(P, B), Cr⁺(aq): -987.7(B), Cr⁺(aq): -42.1(P), Cr⁺(aq): -176.1(P), Cr⁺(aq): -315.4(P), Cr⁺(aq): -51.5(P), Cr⁺(aq): -151.2(P), Cr⁺(aq): -128.1(P), Cr⁺(aq): -144.2(P), HCr⁺(aq): -184.9(P), Cr⁺(aq): -39.9(B), Cr⁺(aq): -49.1(B), Cr⁺(aq): -113.1(S), Cr⁺(aq): -121.1(C)</td>
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<tr>
<td>Cu</td>
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<tr>
<td>Fe</td>
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<td>Ni</td>
<td>Ni⁺(aq): -112.27(P), Ni⁺(aq): -170.15(P), Ni⁺(aq): -51.3(P), Ni⁺(aq): -108.3(P), Ni⁺(aq): -106.9(A), Ni⁺(aq): -11.53(P), Ni⁺(aq): -10.93(N), Ni⁺(aq): -83.5(P), Ni⁺(aq): -19.3(B), Ni⁺(aq): -35.6(N), Ni⁺(aq): -78.0(N)</td>
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<tr>
<td>Pt</td>
<td>Pt⁺(aq): -11.5(P), Pt⁺(aq): -20.0(P), Pt⁺(aq): -16.0(P), Pt⁺(aq): -54.8(P), Pt⁺(aq): -60.9(J), Pt⁺(aq): -17.9(B), Pt⁺(aq): -26.0(I)</td>
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<td></td>
</tr>
<tr>
<td>Ta</td>
<td>Ta⁺(aq): -456.8(B), Ta⁺(aq): -80.5(B)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>Ti⁺(aq): -116.9(P), Ti⁺(aq): -122.7(J), Ti⁺(aq): -212.3(P), Ti⁺(aq): -342.3(P), Ti⁺(aq): -553.9(J), Ti⁺(aq): -116.9(P), Ti⁺(aq): -75.1(J), Ti⁺(aq): -83.6(P), Ti⁺(aq): -228.5(P), Ti⁺(aq): -61.9(J), Ti⁺(aq): -76.1(J), Ti⁺(aq): -88.6(J)</td>
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<td></td>
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<tr>
<td>Zr</td>
<td>Zr⁺(aq): -142.0(P), Zr⁺(aq): -201.5(P), Zr⁺(aq): -287.7(P), Zr⁺(aq): -370.0(P), Zr⁺(aq): -61.7(J), Zr⁺(aq): -94.4(J), Zr⁺(aq): -116.0(J)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* a: gaseous, l: liquid, s: solid, aq: aqueous
* b: units: kcal/mol
* c: References cited are as follows:
(Table 1, continued)

P: Referred from Pourbaix’s Atlas favorite

P': Calculated from Gibbs energy of hydrated oxides of Pourbaix’s Atlas, using the value of Gibbs energy of H2O equal to $-56.7 \text{kcal/mole}$

B: Calculated from Barin et al.’s Data favorite

J: Referred from JANAF Thermochemical Tables favorite

C: Calculated from the stability constants of complexes from the data of “Critical Stability Constants,” using the values of Gibbs energy of I$^-$, IO$_3^-$, etc. of Pourbaix’s Atlas

N: Referred from the NBS “Selected Value of Chemical Thermodynamic Properties”

S: Calculated from the stability constants of complexes from the data of “Stability Constants of Metal-Ion Complexes” favorite

I: Referred from the data of IUPAC’s “Standard Potentials in Aqueous Solution”

Fig. 4 Potential-pH diagram of Fe-I-H$_2$O.
Activities of dissolved iodine compounds are as follows:

\[ \text{---------: 100, \quad ---: 10.} \]
(Note: Stable area of FeI$_2$(aq) is present when above activities are 10 or 100.)

Fig. 5 Potential-pH diagram of Ni-I-H$_2$O.
Activities of dissolved iodine compounds are as follows:

\[ \text{---------: 100, \quad ---: 10.} \]
(Note: Stable area of NiI$_2$(aq) is present when above activities are 10 or 100.)

Fig. 6 Potential-pH diagram of Co-I-H$_2$O.
Activities of dissolved iodine compounds are as follows:

\[ \text{---------: 100, \quad ---: 1.} \]
(Note: Stable area of CoI$_2$(aq) is present when above activities are 1, 10 or 100, and that of Co(IO$_3$)$_2$(s) is present when they are 10 or 100.)

Fig. 7 Potential-pH diagram of Cr-I-H$_2$O.
Activities of dissolved iodine compounds are as follows:

\[ \text{---------: 100, \quad ---: 0.1.} \]
(Note: Stable area of Cr(HIO$_3$)$_2$($^+$)(aq) is present when above activities are 0.1, 1, 10 or 100.)
ly in various data compilations\textsuperscript{10)\textendash 16). Consistency among the values is not necessarily guaranteed when the data from different sources are used. Therefore, we tried to select the data from a single source for each metal, if possible. If not possible, we are obliged to use the data from different sources. In this case, we tried to check if the data for the same compound from different sources have nearly equal values to each other. The adopted data are listed in Table 1 with their sources.

The calculations were done under the assumption that the activity of solid substance be 1.0 and that of dissolved corrosion product be $1.0 \times 10^{-6}$, as is often assumed. The activities of the dissolved iodine compounds ($i.e., I^-, I_3^-, I^+, HIIO_4$, $IO_3^-, HIIO_5^-, IO_2^-, HIIO_5^{2-}$, and $IO_5^{3-}$), are assumed as 0.01, 0.1, 1.0, 10, or 100.*\textsuperscript{6}

4. Results and discussion

Potential-pH diagrams of iron-group metals ($i.e.,$ iron, nickel, and cobalt) are presented in Figs. 4, 5, and 6, respectively. In dilute solution of iodine, where the activities of dissolved iodine compounds are less than 0.1, no areas of predominance of iodides exist on the E-pH diagrams and we can consider the system as if there were no iodine from thermodynamic point of view. In the concentrated iodine solution, where the activities of dissolved iodine compounds are higher than $10^{-7})$, the metal iodides in aqueous state is stable in low pH and rather less-noble region. The redox potential of MgI$_2$-I$_2$-H$_2$O solution (molar ratio is 1: 1: 10) measured on tantalum electrode was about 0.42 volts (vs. NHE) at room temperature\textsuperscript{3}) and the pH value is about 7. Therefore, there is possibility that nickel and cobalt corrode in the form of iodides.

*\textsuperscript{6}) It is difficult to estimate the activity of corrosive species in concentrated solution at high temperature and high pressure such as environments used in the experiments already reported\textsuperscript{3). The experiments were done under several conditions but typical test solution contains 1 mole of MgI$_2$, 0.2 moles of Mg(IO$_3$)$_2$, 4.8 moles of I$_2$, and 9.6 moles of H$_2$O, which corresponds to the concentration of about 70 grams-atom iodine in 1 liter-H$_2$O. We assumed the values as described, for it is considered that the absolute values of activity are not necessary for our purpose to do relative comparison among metals.

*\textsuperscript{7}) As for Co, CoI$_2$(aq), the activity of which is $1 \times 10^{-6}$, is just in equilibrium with Co$^{2+}$ and I$^-$ when the activity of I$^-$ is 1.0, which is presented in Fig. 6.

As for chromium, which is the most common alloying element for ferrous materials and nickel alloys, chromium iodides are less stable than Cr$^{3+}$, Cr$^{3+}$, or Cr(OH)$_3$, etc. and only Cr(HIO$_4$)$_3^{2+}$ shows stable region among iodine-containing species, as shown in Fig. 7. The redox potential and the pH value above mentioned lies in the
stable area of Cr(OH)$_3$ (or hydrated Cr$_2$O$_3$). Therefore, it is expected that Cr may be protective in the concentrated iodine solution, such as in the environments used in our experiments. However, the experiments$^1$ of Cr, Ni-Cr alloys and Incoloy 600 gave negative results$^8$ in solutions with slightly different composition (including more iodine and Mg(IO$_3$)$_2$ than the solution where the redox potential and pH was measured) at high temperature. Rather good (but unstable) protectiveness was observed for Hastelloy-C, which may be attributed to the co-existence of Mo and Cr in that alloy, but the reason is not clear up to now.

Noble metals such as gold, silver, copper and platinum are the typical examples where there is great difference between the systems with and without iodine, as shown in Figs. 8, 9, 10, and 11, respectively. For instance, although Au is stable in the whole region of stability of water in metal-water system$^{10}$, the presence of small amount of iodine (activity is 0.01) dissolves Au in the form of AuI$_2^-$ (aq). Pt corrodes also by forming of PtI$_4$(s), but not of PtI$_4^-$ (aq). The corrosion rate of Pt will be smaller than Au, since the solid iodide film shows protective nature, to some extent, on the surface of Pt. These predictions agree to the experimental data of corrosion rates$^1$.

As for titanium, zirconium, and tantalum, no stable area of iodides are present on the E-pH diagram and the E-pH diagrams of metal-iodine-water system are the same as those of metal-water system, even when the activity of dissolved iodine compounds is 100, thus the results are omitted in this paper. This suggests that these metals are expected to be protective in concentrated iodine solution because tight oxide films (e.g., TiO$_2$, ZrO$_2$·2H$_2$O, and Ta$_2$O$_5$) are thermodynamically more stable than iodides considered.

In summary, thermodynamical prediction at 25°C as described above is fairly in good agreement with the experimental results at high temperature reported before$^1$, when substances listed in table 1 are taken into consideration, though credible thermodynamical data of iodides and iodine complexes are not necessarily available for all the elements considered. From the experimental data, Fe-, Ni-, and Co-alloys and metals as well as Au, Ag, and Pt corrode in the concentrated iodine solutions, but Ti, Zr, and Ta are rather protective. The insufficient stability of passive film of Ti and Zr, compared to Ta, observed in the experiments may be interpreted by further consideration of the temperature dependence of thermodynamic functions and/or unknown complexes of these metals.

5. Conclusion
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construction of the potential-pH diagrams of metal-ion-water system was demonstrated and applied to the metal-iodine-water systems. Thermodynamic data are not always available for each compound to be considered, but the following predications were derived in the present case: (1) Ta, Ti, and Zr are protective in concentrated iodine solution because of oxide film formation; (2) Au, Ag and Pt will corrode because of the formation of iodine complexes or less protective solid iodides. (3) Fe, Ni, and Co will corrode rapidly. There is a possibility of iodide formation in case of Ni and Co in concentrated iodine solutions. These thermodynamic predictions are fairly in good agreement with the experimental results, in spite of the lack of the estimation of the values of thermodynamic functions at high temperature.

Acknowledgement

The authors wish to express their sincere gratitude to Dr. Toshiaki Kodama, National Research Institute of Metals, and Dr. Hideo Hirano, Central Research Institute of Electric Power Industry, for their helpful discussions and informations.

(Received October 29, 1986)

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