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:

Among the four reactions, only the first stage reaction proceeds in aqueous solution. The corrosion behavior of metallic materials in this environment was already studied¹⁾ 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 potenti-

al-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 Brook²⁾ and was followed by several researchers^{3)~7)} for metal-water system. As for the metal-ion-water system, the algorithm proposed by Froning *et al.*⁸⁾ is the only method that has a rigid base among algorithms categorized as a continuum type analysis⁸⁾ (not the 'point by point' analysis), and it has been extensively applied by Chen *et al.*⁸⁾.

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

* 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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Fig. 1 Convex Polygon Method: Consideration of equilibria of a species with other species one by one determines the limit of the a.p. of that species.

(species of the type of $\{Me_{m1}O_{x1}H_{y1}^{z1+}\}$ or $\{W_{w2}O_{x2}H_{y2}^{z2+}\}$), and (2) 'complex' system where the chemical species contain the second element (species of the type of $\{Me_{m3}W_{w3}O_{x3}H_{y3}^{z3+}\}$). 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 'e⁻' 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 $\{Me_{m1}O_{x1}H_{y1}^{z1+}\}$ with $\{Me_{m2}O_{x2}H_{y2}^{z2+}\}$ determines the limit of a.p. of the former substance because of the reaction,

$$= B*[Me_{m2}O_{x2}H_{y2}^{z2+}] + C*[H_2O],$$

where⁸⁾

$$M = (m2/m1)*(y2 - 2*x2) + (2*x1 - y2),$$

$$Z = \{z1 - (m1/m2)*z2\}$$

$$+ (m1/m2)*(y2 - 2*x2) + (2*x1 - y1),$$

$$B = m1/m2, \quad C = x1 - (m1/m2)*x2.$$

The chemical species $\{Me_{m1}O_{x1}H_{y1}^{z1+}\}$ is more stable than $\{Me_{m2}O_{x2}H_{y2}^{z2+}\}$ in the region where the following inequality is satisfied

$$E > E^\circ - (RT/ZF)*M*2.303*pH$$

$$+ (RT/ZF)*2.303*\log\{a_1/a_2\}$$

if $Z > 0$ ^{*1)}. In the above equation, R is gas constant, T is absolute temperature, F is Faraday's constant. a_1 and a_2 are the activities of $\{Me_{m1}O_{x1}H_{y1}^{z1+}\}$ and $\{Me_{m2}O_{x2}H_{y2}^{z2+}\}$, respectively. The value of E° is calculated from the Gibbs energy of the species at T. By considering all of this kind of inequalities which represent the equilibria with other species ($Me_{m3}O_{x3}H_{y3}^{z3+}$, $Me_{m4}O_{x4}H_{y4}^{z4+}$, ...), the a.p. of $\{Me_{m1}O_{x1}H_{y1}^{z1+}\}$ 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-H₂O. The same procedure is valid in the construction of the E-pH diagram of W-H₂O system.

2.2 Area of Predominance of Complex Systems

For the Me-W-H₂O system in which element W has its own E-pH equilibria (e.g. HI, I⁻, and I₂), 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.*³⁾ 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⁻, I₂, ...), (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 ($Me_{m3}W_{w3}O_{x3}H_{y3}^{z3+}$) has an interior angle larger than π radian at the boundaries of the a.p.'s on the E-pH diagrams of Me-H₂O and W-H₂O, as is shown in the example of Fe-S-H₂O system¹⁷⁾.

(a) "Polygon Test"

(b) Arrangement of the order of the vertices

Fig. 2 (a) Polygon Test: When the sum of the interior angles around a certain point between two adjacent vertices of a polygon is 2π radian, that point is an inner point of that polygon, 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 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 $\text{FeI}_2 \cdot 2\text{NH}_3$ is formed).

The algorithm proposed in this paper for determination of the a.p. of the Me-W-O-H compound ($\{\text{Me}_{m3}\text{W}_{w3}\text{O}_{x3}\text{H}_{y3}^{z3+}\}$) is as follows: (1) to determine the common area of the a.p. of Me-O-H compound ($\{\text{Me}_{m1}\text{O}_{x1}\text{H}_{y1}^{z1+}\}$) and the a.p. of W-O-H compound ($\{\text{W}_{w2}\text{O}_{x2}\text{H}_{y2}^{z2+}\}$), (2) to apply the Convex Polygon Method^{*3)} to the determination

of the a.p. of $\{\text{Me}_{m3}\text{W}_{w3}\text{O}_{x3}\text{H}_{y3}^{z3+}\}$ within the area limited in step (1), by considering the reaction with $\{\text{Me}_{m1}\text{O}_{x1}\text{H}_{y1}^{z1+}\}$, $\{\text{Me}_{m4}\text{W}_{w4}\text{O}_{x4}\text{H}_{y4}^{z4+}\}$, $\{\text{Me}_{m5}\text{W}_{w5}\text{O}_{x5}\text{H}_{y5}^{z5+}\}$, $\dots$, and $\{\text{W}_{w2}\text{O}_{x2}\text{H}_{y2}^{z2+}\}$, 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 $\{\text{Me}_{m3}\text{W}_{w3}\text{O}_{x3}\text{H}_{y3}^{z3+}\}$ 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 $\{\text{Me}_{m1}\text{O}_{x1}\text{H}_{y1}^{z1+}\}$ are the inner point of the a.p. of $\{\text{W}_{w2}\text{O}_{x2}\text{H}_{y2}^{z2+}\}$ 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 $\{\text{W}_{w2}\text{O}_{x2}\text{H}_{y2}^{z2+}\}$ are the inner point of the a.p. of $\{\text{Me}_{m1}\text{O}_{x1}\text{H}_{y1}^{z1+}\}$ 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 $\{\text{Me}_{m1}\text{O}_{x1}\text{H}_{y1}^{z1+}\}$ intersect with those of the a.p. of $\{\text{W}_{w2}\text{O}_{x2}\text{H}_{y2}^{z2+}\}$ (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 graphics⁹⁾ is used; that is, if a point is inner point in the polygon, then the sum of the interior angles around that point between two adjacent vertices of the polygon is 2π radian, as shown in Fig. 2 (a). In the step (1-d), the 'principle of maximum interior angle' for convex polygon^{*4)}, shown in Fig. 2 (b), is applied.

The balancing equation used in step(2) for the reaction of $\{\text{Me}_{m3}\text{W}_{w3}\text{O}_{x3}\text{H}_{y3}^{z3+}\}$ and $\{\text{Me}_{m4}\text{W}_{w4}\text{O}_{x4}\text{H}_{y4}^{z4+}\}$ (when $w_4=0$, the latter also represents the Me-O-H compound) is as follows:

where

$$\begin{aligned} \text{M} &= -y_3 - (y_2/w_2) \cdot (m_3 \cdot w_4 / m_4 - w_3) \\ &+ 2 \cdot x_3 + 2 \cdot x_2 \cdot (m_3 \cdot w_4 / m_4 - w_3) / w_2 \\ &- 2 \cdot m_3 \cdot x_4 / m_4 + m_3 \cdot y_4 / m_4, \\ \text{A} &= (m_3 \cdot w_4 / m_4 - w_3) / w_2, \\ \text{Z} &= z_3 + z_2 \cdot (m_3 \cdot w_4 / m_4 - w_3) / w_2 \\ &- m_3 \cdot z_4 / m_4 - y_3 - y_2 \cdot (m_3 \cdot w_4 / m_4 \\ &- w_3) / w_2 + 2 \cdot x_3 + 2 \cdot x_2 \cdot (m_3 \cdot w_4 / m_4 \\ &- w_3) / w_2 - 2 \cdot m_3 \cdot x_4 / m_4 + m_3 \cdot y_4 / m_4, \\ \text{B} &= m_3 / m_4, \end{aligned}$$

*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 $\{\text{Me}_{m1}\text{O}_{x1}\text{H}_{y1}^{z1+}\}$ and $\{\text{W}_{w2}\text{O}_{x2}\text{H}_{y2}^{z2+}\}$, 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.

Fig. 3 Schematic diagram of the process for determination of the area of predominance of Me-W-O-H compound.

(a) E-pH diagram of Fe-H₂O (—) and I-H₂O (-----).

(b) Equilibria of FeI₂ with {Fe₃O₄, FeI₃, or FeI₂⁺} and {I⁻, H⁺, e⁻, and H₂O} give the area of predominance of FeI₂ within the common region of the a.p.'s of Fe₃O₄ and I⁻.

(c) Area of predominance of FeI₂.

$C = x_3 + x_2 \cdot (m_3 \cdot w_4 / m_4 - w_3) / w_2 - m_3 \cdot x_4 / m_4$.
 $\{Me_{m_3}W_{w_3}O_{x_3}H_{y_3}^{z_3+}\}$ is more stable than $\{Me_{m_4}W_{w_4}O_{x_4}H_{y_4}^{z_4+}\}$ in the region which satisfy the following inequality

$$E > E^\circ - (RT/ZF) \cdot M \cdot 2.303 \cdot \text{pH} + (RT/ZF) \cdot 2.303 \cdot \log \{a_3 \cdot a_2^A / a_4^B\}$$

if $Z > 0$ ^(*), where a_3 , a_2 , and a_4 are the activities of $\{Me_{m_3}W_{w_3}O_{x_3}H_{y_3}^{z_3+}\}$, $\{W_{w_2}O_{x_2}H_{y_2}^{z_2+}\}$, and $\{Me_{m_4}W_{w_4}O_{x_4}H_{y_4}^{z_4+}\}$, respectively.

Fig. 3 shows the example of the process to determine the a.p. of FeI₂ assuming the activities of dissolved iodine compounds be 10. Fig. 3 (a)

represents the E-pH diagram of Fe-H₂O and I-H₂O. The quadrangular area in Fig. 3 (b) is the common area of the a.p.'s of Fe₃O₄ in Fe-H₂O system and that of I⁻ in I-H₂O system. Consideration of the equilibria of FeI₂ with {Fe₃O₄, FeI₂⁺, or FeI₃} and {H⁺, I⁻, e⁻ and H₂O} on the above quadrangular area determines the a.p. of FeI₂ within that area^(*). The shaded area, assigned number of which is (1) in Fig. 3 (c), expresses the a.p. of FeI₂ within that area, thus determined. By considering all the pairs of (Fe³⁺, Fe²⁺, etc.) and (I⁻, I₂, IO₃⁻, etc.), the a.p. of FeI₂ is determined as shown in Fig. 3 (c). The areas (2)~(6) in Fig. 3 (c) represents the a.p. of FeI₂ from the pairs of (Fe, I⁻), (Fe²⁺, I⁻), (Fe₂O₃, I₂), and (Fe₂O₃, I⁻), respectively.

2.3 Potential-pH Diagrams of Complex systems

After the completion of steps (1)~(3) in 2.2, the E-pH diagram of Me-W-H₂O is expressed as the overlap of the 'virtual' E-pH diagram of Me-H₂O, which is determined by the algorithm in 2.1 under the assumption that no W species exist in the system, and the a.p.'s of Me-W-O-H compounds determined by the method in 2.2.

That is, (1) The each of a.p. of Me-W-O-H compound is just the same as determined in 2.2, and (2) The a.p. of Me-O-H compound on the E-pH diagram of Me-W-H₂O is the area which is determined by exclusion of the a.p.'s of Me-W-O-H compounds from the a.p. of that Me-O-H compound on the 'virtual' E-pH diagram of Me-H₂O.

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-

^(*) The reactions of FeI₂ with Fe₃O₄, FeI₂⁺, or FeI₃ on the common area of a.p.'s of Fe₃O₄ on Fe-H₂O system and I⁻ on I-H₂O system are as follows:

FeI₂ is stable in the area where the following inequalities, which correspond to the above reactions, are simultaneously satisfied.

$$\begin{aligned} E < 1.5873 - 0.2367 \cdot \text{pH}, \\ E < 0.716, \quad E < 0.710. \end{aligned}$$

Table 1. List of values of Gibbs energy.

ELEM.	SUBSTANCES(state* ^a): ADOPTED DATA* ^b) (ref.* ^c) {OTHER DATA* ^b) (ref.* ^c)}, ..., ..., ...
H	H ₂ (g): 0.0, H ₂ O(l): -56.7 (P, N, B)
I	I ₂ (s): 0.0, I ⁻ (aq): -12.35(P), I ₃ ⁻ (aq): -12.31(P), I ⁺ (aq): 31.29(P), HIO(aq): -23.5(P), IO ⁻ (aq): -8.5(P), HIO ₃ (aq): -33.34(P), IO ₃ ⁻ (aq): -32.25(P), HIO ₄ (aq): -15.02(P), IO ₄ ⁻ (aq): -12.7(P), HIO ₅ ²⁻ (aq): -58.11(P), IO ₅ ³⁻ (aq): -43.11(P)
Ag	Ag(s): 0.0, AgOH(s): 12.7(P), AgOH(aq): -22.0(N), Ag ₂ O ₂ (s): 6.6(N), Ag ₂ O(s): -2.68(N) {-2.59(P, B)}, Ag ₂ O ₃ (s): 29.0(N), AgO ⁻ (aq): -5.5(P), Ag ⁺ (aq): 18.4(N, P), Ag ²⁺ (aq): 64.1(N, P), Ag(OH) ₂ ⁻ (aq): -62.2(N), AgI(s): -15.8(N, C) {-15.7(S)}, AgI(aq): -2.9(N, C), AgIO ₃ (s): -22.4(N, S), AgI ₂ ⁻ (aq): -20.8(N) {-21.2(C)}, AgI ₃ ²⁻ (aq): -36.8(N) {-37.8(C)}, AgI ₄ ³⁻ (aq): -50.1(N) {-50.5(C)}, AgHIO ₃ ⁺ (aq): -15.8(C), Ag(HIO ₃) ₂ ⁺ (aq): -50.8(C)
Au	Au(s): 0.0, Au(OH) ₃ (aq): -75.8(I), Au(OH) ₃ (s): -67.8(I), Au ⁺ (aq): 42.0(I), Au ³⁺ (aq): 105.2(I), AuO ₃ ³⁻ (aq): -12.4(I), HAuO ₂ ²⁻ (aq): -33.9(I), H ₂ AuO ₃ ⁻ (aq): -52.1(I), AuI(s): -0.12(I), AuI ₂ ⁻ (aq): -11.4(I), AuI ₄ ⁻ (aq): -10.8(I)
Co	Co(s): 0.0, CoO(s): -51.2(N) {-51.4(B)}, Co(OH) ₂ (aq): -100.8(N), Co(OH) ₂ (s): -109.5(N) {-109.0(P)}, Co ₃ O ₄ (s): -185.0(N) {-188.0(B)}, Co(OH) ₃ (s): -142.6(P), CoO ₂ (s): -51.8(P), Co ²⁺ (aq): -13.0(N), Co ³⁺ (aq): 32.0(N), HCoO ₂ ⁻ (aq): -97.4(N), CoI ₂ (s): -21.7(B), CoI ₂ (aq): -37.7(N), Co(IO ₃) ₂ (s): -85.0(S), Co(IO ₃) ₂ (aq): -74.2(N), Co(IO ₃) ₂ ·2H ₂ O(s): -190.2(N)
Cr	Cr(s): 0.0, Cr(OH) ₂ (s): -140.5(P'), Cr(OH) ₃ (s): -215.3(P'), Cr(OH) ₄ (s): -242.4(P'), Cr ₂ O ₃ (s): -250.2(P) {-250.5(B)}, CrO ₂ (s): -126.3(B), Cr ₃ O ₁₂ (s): -626.6(B), CrO ₃ (s): -120.0(P, B), Cr ₈ O ₂₁ (s): -987.7(B), Cr ²⁺ (aq): -42.1(P), CrO ₄ ²⁻ (aq): -176.1(P), Cr ₂ O ₇ ²⁻ (aq): -315.4(P), Cr ³⁺ (aq): -51.5(P), Cr(OH) ₂ ⁺ (aq): -151.2(P), CrO ₂ ⁻ (aq): -128.1(P), CrO ₃ ³⁻ (aq): -144.2(P), HCrO ₄ ⁻ (aq): -184.9(P), CrI ₂ (s): -39.9(B), CrI ₃ (a): -49.1(B), Cr(IO ₃) ₂ ⁺ (aq): -113.1(S), Cr(HIO ₃) ₂ ³⁺ (aq): -121.1(C)
Cu	Cu(s): 0.0, Cu ⁺ (aq): 12.0(N), Cu ²⁺ (aq): 15.7(N), Cu(OH) ₂ (s): -85.3(P'), Cu(OH) ₂ (aq): -59.5(N), CuO(s): -31.0(N), Cu ₂ O(s): -35.0(N), HCuO ₂ ⁻ (aq): -61.8(N), CuO ₂ ²⁻ (aq): -43.9(N), CuI(s): -16.6(N), Cu(IO ₃) ₂ (s): -57.3(S), Cu(IO ₃) ₂ (aq): -45.5(N), Cu(IO ₃) ₂ ·H ₂ O(s): -112.0(N), Cu(IO ₃) ₂ ·3Cu(OH) ₂ (s): -160.0(N), Cu(HIO ₃) ₂ (s): -60.9(C)
Fe	Fe(s): 0.0, FeO(s): -60.1(J), Fe(OH) ₂ (s): -116.3(N) :-117.6(J);, Fe ₃ O ₄ (s): -242.7(N) {-243.2(J)}, Fe ₂ O ₃ (s): -177.4(N) {-177.7(J)}, Fe(OH) ₃ (s): -166.53(N) {-168.6(J)}, Fe ²⁺ (aq): -18.9(N), Fe ³⁺ (aq): -1.1(N), HFeO ₂ ⁻ (aq): -90.3(N), FeOH ²⁺ (aq): -54.8(N), Fe(OH) ₂ ⁺ (aq): -104.7(N), Fe(OH) ₃ ⁻ (aq): -147.0(N), Fe(OH) ₄ ²⁻ (aq): -184.0(N), FeI ²⁺ (aq): -16.0(N), FeI ₂ (aq): -43.5(N), FeI ₂ (s): -26.7(J), FeI ₃ (aq): -38.1(N)
Ni	Ni(s): 0.0, Ni ₂ O ₃ (s): -112.27(P), Ni ₃ O ₄ (s): -170.15(P), NiO(s): -51.3(P) {-50.6(N), -50.8(B)}, NiO ₂ (s): -51.42(P), Ni(OH) ₂ (s): -108.3(P') {-106.9(N)}, Ni ²⁺ (aq): -11.53(P) {-10.9(N)}, HNiO ₂ ⁻ (aq): -83.5(P, N), NiI ₂ (s): -19.3(B), NiI ₂ (aq): -35.6(N), Ni(IO ₃) ₂ (s): -78.0(N)
Pt	Pt(s): 0.0, PtO(s): -11.5(P), PtO ₂ (s): -20.0(P), PtO ₃ (s): -16.0(P), Pt ²⁺ (aq): 54.8(P) {60.9(I)}, PtI ₄ (s): -17.9(B), PtI ₆ ²⁻ (aq): -26.0(I)
Ta	Ta(s): 0.0, Ta ₂ O ₅ (s): -456.8(B), TaI ₅ (s): -80.5(B)
Ti	Ti(s): 0.0, TiO(s): -116.9(P) {-122.7(J)}, TiO ₂ (Rutile) (s): -212.3(P) {-212.6(J)}, Ti ₂ O ₃ (s): -342.3(P) {-342.7(J)}, Ti ₃ O ₅ (s): -553.1(P) {-553.9(J)}, TiO ²⁺ (aq): -138.0(P), Ti ²⁺ (aq): -75.1(P), Ti ³⁺ (aq): -83.6(P), HTiO ₃ ⁻ (aq): -228.5(P), TiO ₂ ²⁺ (aq): -111.7(P), TiI ₂ (s): -61.9(J), TiI ₃ (s): -76.1(J), TiI ₄ (s): -88.6(J)
Zr	Zr(s): 0.0, Zr ⁴⁺ (aq): -142.0(P), ZrO ²⁺ (aq): -201.5(P), HZrO ₃ ⁻ (aq): -287.7(P), ZrO ₂ (s): -248.5(P, J), ZrO ₂ ·2H ₂ O(s): -370.0(P'), ZrI ₂ (s): -61.7(J), ZrI ₃ (s): -94.4(J), ZrI ₄ (s): -116.0(J)

^a) g: 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 Atlas¹⁰⁾

P': Calculated from Gibbs energy of hydrated oxides of Pourbaix's Atlas¹⁰⁾, using the value of Gibbs energy of H₂O equal to -56.7 kcal/mole

B: Calculated from Barin *et al.*'s Data¹¹⁾

J: Referred from JANAF Thermochemical Tables¹²⁾

C: Calculated from the stability constants of complexes from the data of "Critical Stability Constants"¹³⁾, using the values of Gibbs energy of I⁻, IO₃⁻, *etc.* of Pourbaix's Atlas¹⁰⁾

N: Referred from the NBS "Selected Value of Chemical Thermodynamic Properties"¹⁴⁾

S: Calculated from the stability constants of complexes from the data of "Stability Constants of Metal-Ion Complexes"¹⁵⁾

I: Referred from the data of IUPAC's "Standard Potentials in Aqueous Solution"¹⁶⁾

Fig. 4 Potential-pH diagram of Fe-I-H₂O.

Activities of dissolved iodine compounds are as follows:

.....: 100, ----: 10.

(Note: Stable area of FeI₂(aq) is present when above activities are 10 or 100.)

Fig. 6 Potential-pH diagram of Co-I-H₂O.

Activities of dissolved iodine compounds are as follows:

.....: 100, ----: 1.

(Note: Stable area of CoI₂(aq) is present when above activities are 1, 10 or 100, and that of Co(IO₃)₂(s) is present when they are 10 or 100.)

Fig. 5 Potential-pH diagram of Ni-I-H₂O.

Activities of dissolved iodine compounds are as follows:

.....: 100, ----: 10.

(Note: Stable area of NiI₂(aq) is present when above activities are 10 or 100.)

Fig. 7 Potential-pH diagram of Cr-I-H₂O.

Activities of dissolved iodine compounds are as follows:

.....: 100, ----: 0.1.

(Note: Stable area of Cr(HIO₃)₂³⁺(aq) is present when above activities are 0.1, 1, 10 or 100.)

ly in various data compilations^{(10)~(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 1.0×10^{-6} , as is often assumed. The activities of the dissolved iodine compounds (*i.e.*, I^- , I_3^- , I^+ , HIO , IO^- , HIO_3 , IO_3^- , HIO_4 , IO_4^- , HIO_5^{2-} , and IO_5^{3-}), are assumed as 0.01, 0.1, 1, 10, or 100.*⁽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_2O solution (molar ratio is 1: 1: 10) measured on tantalum electrode was about 0.42 volts (*vs.* NHE) at room temperature⁽¹⁾ and the pH value is about 7. Therefore, there is possibility that nickel and cobalt corrode in the form of iodides.

*⁽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⁽¹⁾. 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_2O , which corresponds to the concentration of about 70 grams-atom iodine in 1 liter- H_2O . 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.

*⁽⁷⁾ As for Co, $CoI_2(aq)$, the activity of which is 1×10^{-6} , is just in equilibrium with Co^{2+} and I^- when the activity of I^- is 1.0, which is presented in Fig. 6.

Fig. 8 Potential-pH diagram of Au-I- H_2O .

Activities of dissolved iodine compounds are as follows:

.....: 100, ----: 0.01.

(Note: Stable areas of $Au(s)$ and AuI_2^- are present when above activities are 0.01, 0.1, 1, 10 or 100.)

Fig. 9 Potential-pH diagram of Ag-I- H_2O .

Activities of dissolved iodine compounds are as follows:

.....: 100, ----: 0.01.

(Note: Stable area of $AgI(s)$ is present when above activities are 0.01, 0.1, 1, 10 or 100. That of $AgI_3^{2-}(aq)$ is present when they are 0.1, 1, 10 or 100. Those of $AgI_4^{3-}(aq)$, $AgIO_3(s)$, and $Ag(HIO_3)_2^+(aq)$ are present when they are 1, 10 or 100.)

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^{2+} , or $Cr(OH)_3$, etc. and only $Cr(HIO_3)_2^{3+}$ shows stable region among iodine-containing species, as shown in Fig. 7. The redox potential and the pH value above mentioned lies in the

Fig. 10 Potential-pH diagram of Cu-I-H₂O.

Activities of dissolved iodine compounds are as follows:

.....: 100, ----: 0.01.

(Note: Stable area of CuI(s) is present when above activities are 0.01, 0.1, 1, 10 or 100. That of Cu(OH)₂(s) is present when they are 1, 10 or 100.)

Fig. 11 Potential-pH diagram of Pt-I-H₂O.

Activities of dissolved iodine compounds are as follows:

.....: 100, ----: 0.01.

(Note: Stable area of PtI₄(s) is present when above activities are 0.01, 0.1, 1, 10 or 100.)

stable area of Cr(OH)₃ (or hydrated Cr₂O₃). 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 experiments¹⁾ of Cr, Ni-Cr alloys and Incoloy

600 gave negative results^{*8)} in solutions with slightly different composition (including more iodine and Mg(IO₃)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 system¹⁰⁾, the presence of small amount of iodine (activity is 0.01) dissolves Au in the form of AuI₂⁻(aq). Pt corrodes also by forming of PtI₄(s), but not of PtI₆²⁻(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 rates¹⁾.

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., TiO₂, ZrO₂·2H₂O, and Ta₂O₅) 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 before¹⁾, 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

An improved algorithm for computer-aided

*8) The protectiveness of Cr metal in that solution could not be determined definitely in the experiment, for the Cr plate tested broke down perhaps because of embrittlement of grain boundary.

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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