

**POTENTIAL-pH DIAGRAMS FOR THE SYSTEMS
Ir-H₂O-Cl⁻, Pt-H₂O-Cl⁻, AND Pd-H₂O-Cl⁻ AT 25°C**

Tomáš LOUČKA and Zdenko TERNBACH

Research Institute of Inorganic Chemistry, 400 60 Ústí nad Labem

Received June 27, 1989

Accepted August 30, 1989

On the basis of available thermodynamic data, potential-pH diagrams have been calculated for the systems Ir-H₂O-Cl⁻, Pt-H₂O-Cl⁻, and Pd-H₂O-Cl⁻ in a 264 g/l NaCl aqueous solution at 25°C.

The potential-pH diagrams for the systems Ir-H₂O, Pt-H₂O, and Pd-H₂O have been known for a number of years. Because of potential application of Ir, Pt and Pd oxide layers to activated titanium anodes for making chlorine and caustic soda, it is of interest to investigate the thermodynamic stability of the layers in chloride medium. While the potential-pH diagram for the system Ru-H₂O-Cl⁻ has been reported¹, no data are available in the literature for the diagrams of Ir-H₂O-Cl⁻, Pt-H₂O-Cl⁻, and Pd-H₂O-Cl⁻.

The calculations were made on the basis of the equations summarized in Table I. The formation of PdH₂ was not considered. The values used for the standard Gibbs free energies of water and Cl⁻ were -236.81 kJ/mol and -131.26 kJ/mol, respectively. The oxides listed in Table I are for the most part called hydrated oxides in the literature.

The potential-pH diagrams were calculated on the basis of the equations summarized in Tables II to IV. Both the equations and the diagrams were evaluated for a temperature of 25°C, and take into consideration only the compounds listed Table I.

The following simplifications were used in the calculations: *a*) the Cl⁻ concentration was considered for the case of a 264 g/l NaOH solution ($\gamma_{\pm, m} = 0.885$, $a(\text{Cl}^-) = 4.425$ (ref.⁴), $a(\text{H}_2\text{O}) = 0.806$ (ref.⁵)), which is close to the conditions of industrial electrolysis; *b*) a value of 10^{-6} was taken for the activities of ions other than Cl⁻.

The resulting diagrams are depicted in Figs 1 to 3. Also plotted in the diagrams is the value of the equilibrium potential of chlorine electrode, $E_r(\text{Cl}_2/\text{Cl}^-) = 1.3113$ V, calculated for $a(\text{Cl}_2) = 1$ and $a(\text{Cl}^-) = 4.425$.

The diagram for the system Ir-H₂O-Cl⁻ is very similar to that for Ru-H₂O-Cl⁻ (ref.¹). For Ru, the region of RuO₂ stability at the equilibrium potential of chlorine

evolution spans a range of pH values from 2.3 to 3.0. For Ir under otherwise the same conditions, this range extends from 4.0 to 4.5.

The diagrams for the systems $\text{Pt-H}_2\text{O-Cl}^-$ and $\text{Pd-H}_2\text{O-Cl}^-$ show a certain degree of similarity. For Pt, only PtO_3 is stable at the equilibrium potential of chlorine evolution at $\text{pH} > 5$. In the case of Pd, PdO_2 is stable in the range $4.7 < \text{pH} < 12$ and PdO_3 at $\text{pH} > 12$.

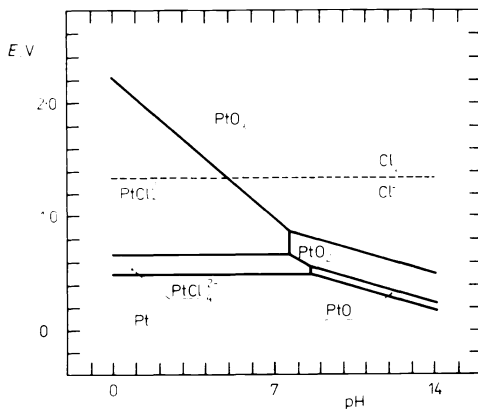


FIG. 1

Potential-pH diagram for the $\text{Pt-H}_2\text{O-Cl}^-$ system at 25°C in a solution of 264 g l^{-1} NaCl . Activities of the other ions are 10^{-6} .

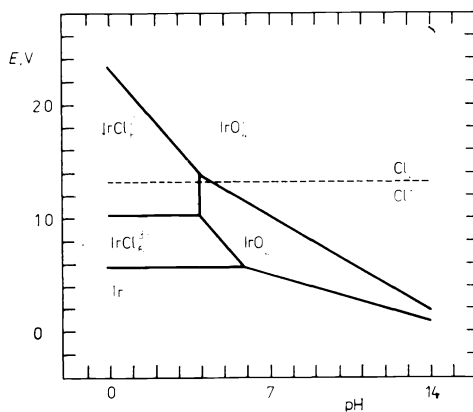


FIG. 2

Potential-pH diagram for the $\text{Ir-H}_2\text{O-Cl}^-$ system at 25°C in a solution of 264 g l^{-1} NaCl . Activities of the other ions are 10^{-6} .

TABLE I
Standard Gibbs free energies of Pt, Ir, and Pd compounds at 25°C

Compound	ΔG_{298}^0 , kJ/mol	Refs
PtO (s)	-48.19	2
PtO ₂ (s)	-83.74	2
PtO ₃ (s)	-66.99	2
Pt ²⁺ (aq)	229.44	2
PtCl ₄ ²⁻ (aq)	-384.77	3
PtCl ₆ ²⁻ (aq)	-515.40	3
Pt(OH) ₂ (s)	-285.54	3
Ir ₂ O ₃ (s)	-175.85	2
IrO ₂ (s)	-117.23	2, 3
Ir ³⁺ (aq)	334.94	2
IrO ₄ ²⁻ (aq)	-196.78	2
IrCl ₆ ³⁻ (aq)	-563.96	3
IrCl ₆ ²⁻ (aq)	-465.57	3
PdO (s)	-60.29	2, 3
PdO ₂ (s)	-53.67	2
PdO ₃ (s)	100.90	2
Pd(OH) ₂ (s)	-301.45	3
Pd(OH) ₄ (s)	-527.54	3
PdCl ₄ ²⁻ (aq)	-404.86	3
PdCl ₆ ²⁻ (aq)	-417.01	3

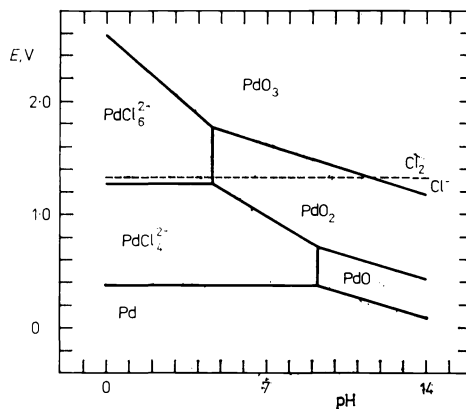


FIG. 3
Potential-pH diagram for the Pd-H₂O-Cl⁻ system at 25°C in a solution of 264 g l⁻¹ NaCl. Activities of the other ions are 10⁻⁶

TABLE II

Reactions and the corresponding equations used to set up the potential-pH diagram for the system Pt-H₂O-Cl⁻ at 25°C. The square bracket indicates the activity of the ion

System No.	Reaction/Equation
1	$\text{Pt(s)} + 4 \text{Cl}^{\text{-}}(\text{aq}) \rightleftharpoons \text{PtCl}_4^{2\text{-}}(\text{aq}) + 2 \text{e}$ $E_r(\text{PtCl}_4^{2\text{-}}/\text{Pt}) = 0.727 + 0.0296 \log \frac{[\text{PtCl}_4^{2\text{-}}]}{[\text{Cl}^{\text{-}}]^4}$
2	$\text{Pt(s)} + \text{H}_2\text{O} \rightleftharpoons \text{PtO(s)} + 2 \text{H}^+(\text{aq}) + 2 \text{e}$ $E_r(\text{PtO}/\text{Pt}) = 0.977 - 0.0296 \log [\text{H}_2\text{O}] - 0.0591 \text{ pH}$
3	$\text{PtCl}_4^{2\text{-}}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{PtO(s)} + 4 \text{Cl}^{\text{-}}(\text{aq}) + 2 \text{H}^+(\text{aq})$ $2 \text{ pH} = 8.470 + \log \frac{[\text{Cl}^{\text{-}}]^4}{[\text{PtCl}_4^{2\text{-}}] [\text{H}_2\text{O}]}$
4	$\text{PtCl}_4^{2\text{-}}(\text{aq}) + 2 \text{Cl}^{\text{-}}(\text{aq}) \rightleftharpoons \text{PtCl}_6^{2\text{-}}(\text{aq}) + 2 \text{e}$ $E_r(\text{PtCl}_6^{2\text{-}}/\text{PtCl}_4^{2\text{-}}) = 0.683 + 0.0296 \frac{[\text{PtCl}_6^{2\text{-}}]}{[\text{PtCl}_4^{2\text{-}}] [\text{Cl}^{\text{-}}]^2}$
5	$\text{PtCl}_4^{2\text{-}}(\text{aq}) + 2 \text{H}_2\text{O} \rightleftharpoons \text{PtO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 4 \text{Cl}^{\text{-}}(\text{aq}) + 2 \text{e}$ $E_r(\text{PtO}_2/\text{PtCl}_4^{2\text{-}}) = 1.293 + 0.0296 \frac{[\text{Cl}^{\text{-}}]^4}{[\text{PtCl}_4^{2\text{-}}] [\text{H}_2\text{O}]^2} - 0.1183 \text{ pH}$
6	$\text{PtO}_2(\text{s}) + \text{H}_2\text{O} \rightleftharpoons \text{PtO}_3(\text{s}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}$ $E_r(\text{PtO}_3/\text{PtO}_2) = 1.314 - 0.0296 \log [\text{H}_2\text{O}] - 0.0591 \text{ pH}$
7	$\text{PtCl}_6^{2\text{-}}(\text{aq}) + 3 \text{H}_2\text{O} \rightleftharpoons \text{PtO}_3(\text{s}) + 6 \text{H}^+(\text{aq}) + 6 \text{Cl}^{\text{-}}(\text{aq}) + 2 \text{e}$ $E_r(\text{PtO}_3/\text{PtCl}_6^{2\text{-}}) = 1.924 + 0.0296 \log \frac{[\text{Cl}^{\text{-}}]^6}{[\text{PtCl}_6^{2\text{-}}] [\text{H}_2\text{O}]^3} +$ $- 0.1774 \text{ pH}$
8	$\text{PtO(s)} + \text{H}_2\text{O} \rightleftharpoons \text{PtO}_2(\text{s}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}$ $E_r(\text{PtO}_2/\text{PtO}) = 1.043 - 0.0296 \log [\text{H}_2\text{O}] - 0.0591 \text{ pH}$
9	$\text{PtCl}_6^{2\text{-}}(\text{aq}) + 2 \text{H}_2\text{O} \rightleftharpoons \text{PtO}_2(\text{s}) + 6 \text{Cl}^{\text{-}}(\text{aq}) + 4 \text{H}^+(\text{aq})$ $4 \text{ pH} = 20.623 + \log \frac{[\text{Cl}^{\text{-}}]^6}{[\text{PtCl}_6^{2\text{-}}] [\text{H}_2\text{O}]^2}$

TABLE III

Reactions and the corresponding equations used to set up the potential-pH diagram for the system Ir-H₂O-Cl⁻ at 25°C. The square bracket indicates the activity of the ion

System No.	Reaction/Equation
1	$\text{Ir(s)} + 2 \text{H}_2\text{O} \rightleftharpoons \text{IrO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}$ $E_r(\text{IrO}_2/\text{Ir}) = 0.923 - 0.0296 \log [\text{H}_2\text{O}] - 0.0591 \text{ pH}$
2	$\text{IrCl}_6^{3-}(\text{aq}) \rightleftharpoons \text{IrCl}_6^{2-}(\text{aq}) + \text{e}$ $E_r(\text{IrCl}_6^{2-}/\text{IrCl}_6^{3-}) = 1.020 + 0.0591 \log \frac{[\text{IrCl}_6^{2-}]}{[\text{IrCl}_6^{3-}]}$
3	$\text{Ir(s)} + 6 \text{Cl}^-(\text{aq}) \rightleftharpoons \text{IrCl}_6^{3-}(\text{aq}) + 3 \text{e}$ $E_r(\text{IrCl}_6^{3-}/\text{Ir}) = 0.772 + 0.0197 \log \frac{[\text{IrCl}_6^{3-}]}{[\text{Cl}^-]^6}$
4	$\text{IrCl}_6^{3-}(\text{aq}) + 2 \text{H}_2\text{O} \rightleftharpoons \text{IrO}_2(\text{s}) + 6 \text{Cl}^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + \text{e}$ $E_r(\text{IrO}_2/\text{IrCl}_6^{3-}) = 1.376 + 0.0591 \log \frac{[\text{Cl}^-]^6}{[\text{IrCl}_6^{3-}] [\text{H}_2\text{O}]^2} - 0.2366 \text{ pH}$
5	$\text{IrCl}_6^{2-}(\text{aq}) + 2 \text{H}_2\text{O} \rightleftharpoons \text{IrO}_2(\text{s}) + 6 \text{Cl}^-(\text{aq}) + 4 \text{H}^+(\text{aq})$ $4 \text{ pH} = 6.026 + \log \frac{[\text{Cl}^-]^6}{[\text{IrCl}_6^{2-}] [\text{H}_2\text{O}]^2}$
6	$\text{IrO}_2(\text{s}) + 2 \text{H}_2\text{O} \rightleftharpoons \text{IrO}_4^{2-}(\text{aq}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}$ $E_r(\text{IrO}_4^{2-}/\text{IrO}_2) = 2.042 + 0.0296 \log \frac{[\text{IrO}_4^{2-}]}{[\text{H}_2\text{O}]^2} - 0.1183 \text{ pH}$
7	$\text{IrCl}_6^{2-}(\text{aq}) + 4 \text{H}_2\text{O} \rightleftharpoons \text{IrO}_4^{2-}(\text{aq}) + 8 \text{H}^+(\text{aq}) + 6 \text{Cl}^-(\text{aq}) + 2 \text{e}$ $E_r(\text{IrO}_4^{2-}/\text{IrCl}_6^{2-}) = 2.220 + 0.0296 \log \frac{[\text{IrO}_4^{2-}] [\text{Cl}^-]^6}{[\text{IrCl}_6^{2-}] [\text{H}_2\text{O}]^4} +$ $- 0.2366 \text{ pH}$

TABLE IV

Reactions and the corresponding equations used to set up the potential-pH diagram for the system Pd-H₂O-Cl⁻ at 25°C. The square bracket indicates the activity of the ion

System No.	Reaction/Equation
1	$\text{Pd(s)} + \text{H}_2\text{O} \rightleftharpoons \text{PdO(s)} + 2 \text{H}^+(\text{aq}) + 2 \text{e}$ $E_r(\text{PdO/Pd}) = 0.915 - 0.0296 \log [\text{H}_2\text{O}] - 0.0591 \text{ pH}$
2	$\text{Pd(s)} + 4 \text{Cl}^-(\text{aq}) \rightleftharpoons \text{PdCl}_4^{2-}(\text{aq}) + 2 \text{e}$ $E_r(\text{PdCl}_4^{2-}/\text{Pd}) = 0.623 + 0.0296 \log \frac{[\text{PdCl}_4^{2-}]}{[\text{Cl}^-]^4}$
3	$\text{PdO(s)} + \text{H}_2\text{O} \rightleftharpoons \text{PdO}_2(\text{s}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}$ $E_r(\text{PdO}_2/\text{PdO}) = 1.261 - 0.0296 \log [\text{H}_2\text{O}] - 0.0591 \text{ pH}$
4	$\text{PdO}_2(\text{s}) + \text{H}_2\text{O} \rightleftharpoons \text{PdO}_3(\text{s}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}$ $E_r(\text{PdO}_3/\text{PdO}_2) = 2.028 - 0.0296 \log [\text{H}_2\text{O}] - 0.0591 \text{ pH}$
5	$\text{PdCl}_4^{2-}(\text{aq}) + 2 \text{Cl}^-(\text{aq}) \rightleftharpoons \text{PdCl}_6^{2-}(\text{aq}) + 2 \text{e}$ $E_r(\text{PdCl}_6^{2-}/\text{PdCl}_4^{2-}) = 1.297 + 0.0296 \log \frac{[\text{PdCl}_6^{2-}]}{[\text{PdCl}_4^{2-}][\text{Cl}^-]^2}$
6	$\text{PdCl}_4^{2-}(\text{aq}) + 2 \text{H}_2\text{O} \rightleftharpoons \text{PdO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 4 \text{Cl}^-(\text{aq}) + 2 \text{e}$ $E_r(\text{PdO}_2/\text{PdCl}_4^{2-}) = 1.553 + 0.0296 \log \frac{[\text{Cl}^-]^4}{[\text{PdCl}_4^{2-}][\text{H}_2\text{O}]^2}$
7	$\text{PdCl}_6^{2-}(\text{aq}) + 3 \text{H}_2\text{O} \rightleftharpoons \text{PdO}_3(\text{s}) + 6 \text{H}^+(\text{aq}) + 6 \text{Cl}^-(\text{aq}) + 2 \text{e}$ $E_r(\text{PdO}_3/\text{PdCl}_6^{2-}) = 2.284 + 0.0296 \log \frac{[\text{Cl}^-]^6}{[\text{PdCl}_6^{2-}][\text{H}_2\text{O}]^3} +$ $- 0.1774 \text{ pH}$
8	$\text{PdCl}_6^{2-}(\text{aq}) + 2 \text{H}_2\text{O} \rightleftharpoons \text{PdO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 6 \text{Cl}^-(\text{aq})$ $4 \text{ pH} = 8.654 + \log \frac{[\text{Cl}^-]^6}{[\text{PdCl}_6^{2-}][\text{H}_2\text{O}]^2}$
9	$\text{PdCl}_4^{2-}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{PdO(s)} + 2 \text{H}^+(\text{aq}) + 4 \text{Cl}^-(\text{aq})$ $2 \text{ pH} = 9.870 + \log \frac{[\text{Cl}^-]^4}{[\text{PdCl}_4^{2-}][\text{H}_2\text{O}]}$

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Translated by M. Škubalová.