

THE POTENTIAL-pH DIAGRAMS DEPICTING THE HYDROGEN CHEMISORPTION IN THE Pt-H₂O, Ir-H₂O, AND Rh-H₂O SYSTEMS AT 25 °C

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Thermodynamic data for the chemisorption of hydrogen on the Pt, Ir, and Rh electrodes were evaluated from data in the literature. On the basis of these data, the potential-pH diagrams were calculated for the Pt-H₂O, Ir-H₂O, and Rh-H₂O systems describing the hydrogen chemisorption. For the hydrogen chemisorption, the surface was considered to be uniformly inhomogeneous.

The principle and employment of the potential-pH diagrams commonly denoted as the Pourbaix diagrams, is well-known¹. Until recently, the potential-pH diagrams have been plotted only for three-dimensional compounds. Lately some works have appeared² which in these diagrams plot even the regions of existence of adsorbed species. A potential-pH diagram was made up depicting the sulfur chemisorption on platinum² and on iron³ and the sulfur and oxygen chemisorption on nickel⁴. Thermodynamic data for the chemisorption were mostly taken over from the measurement of chemisorption in the gas phase. In the calculations, they considered the surface energetically homogeneous and/or the surface on which the chemisorption in terms of the Langmuir isotherm took place. In case of the sulfur chemisorption on platinum in aqueous solutions, the hydrogen chemisorption² was not considered.

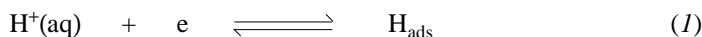
It may be assumed that metals in aqueous medium will exhibit more stability domains of adsorbed species in the potential-pH diagram. With platinum, e.g., it is to be assumed that the stability domain of chemisorbed hydrogen, chemisorbed oxygen and/or further species present in solution, will be shown. For a number of metals, the adsorption will take place according to other isotherms than the Langmuir one.

With the aim to obtain a more complex potential-pH diagram, in the first approximation, the diagram was plotted for the Pt-H₂O, Ir-H₂O, and Rh-H₂O systems considering the hydrogen chemisorption on the surface uniformly inhomogeneous. The thermodynamic data for the hydrogen chemisorption were obtained from electrochemical measurements^{5,6}.

RESULTS AND DISCUSSION

Hydrogen Chemisorption on Uniformly Inhomogeneous Surface

For the hydrogen chemisorption on the Pt, Ir, and Rh electrodes, the reaction



is considered. The dividing of the surface into elements ds is assumed. These elements are so small that the relation

$$\mu_{\text{H},s} = \mu_{\text{H},s}^0 + RT \ln \frac{\Theta_s}{1 - \Theta_s} \quad (2)$$

holds for them, where Θ_s is the relative coverage of element ds with chemisorbed hydrogen, $\mu_{\text{H},s}$ is the chemical potential of chemisorbed hydrogen on element ds and $\mu_{\text{H},s}^0$ is the standard chemical potential of chemisorbed hydrogen on element ds (i.e., the chemical potential of chemisorbed hydrogen on element ds at $\Theta_s = 0.5$). For the uniformly inhomogeneous surface, the relation

$$\mu_{\text{H},s}^0 = \mu_{\text{H},0}^0 + (\mu_{\text{H},1}^0 - \mu_{\text{H},0}^0) s \quad (3)$$

holds, where s changes from 0 to 1, and $\mu_{\text{H},0}^0$ stands for the standard chemical potential of chemisorbed hydrogen on element ds with the highest adsorptivity ($s = 0$) and $\mu_{\text{H},1}^0$ is the standard chemical potential of chemisorbed hydrogen on element ds with lowest adsorptivity ($s = 1$). The total surface coverage can be found by integration

$$\Theta_{\text{H}} = \int_0^1 \Theta_s ds = \frac{1}{f} \ln \frac{1 + \beta}{1 + \beta \exp(-f)}, \quad (4)$$

where f is the surface inhomogeneity coefficient defined by the relation

$$f = \frac{\mu_{\text{H},1}^0 - \mu_{\text{H},0}^0}{RT} \quad (5)$$

and further

$$\beta = \exp\left(\frac{\mu_{H,s} - \mu_{H,0}^0}{RT}\right) \quad (6)$$

holds. From Eqs (4) and (6), it is then possible to derive the relation^{7,8}

$$\mu_H = \mu_{H,0}^0 + RT \ln \frac{\exp(f\Theta_H) - 1}{1 - \exp[-f(1 - \Theta_H)]} \quad (7)$$

The Nernst equation for reaction (1) can be then written in the form

$$E = E^0 - \frac{RT}{F} \ln \frac{\exp(f\Theta_H) - 1}{1 - \exp[-f(1 - \Theta_H)]} - \frac{RT}{F} 2.30258 \text{ pH} \quad (8)$$

where

$$E^0 = -\frac{\mu_{H,0}^0 - \mu_{H^+}^0}{F} \quad (9)$$

It follows from the above-mentioned that to construct the dependence of potential on pH for the given surface coverage with chemisorbed hydrogen, it is necessary to know the surface inhomogeneity coefficient and the value of $\mu_{H,0}^0$.

If f is sufficiently great, Eq. (8) for mean values of coverage $0.2 < \Theta_H < 0.8$ turns to the relation

$$E = E^0 - \frac{RT}{F} f \Theta_H - \frac{RT}{F} 2.30258 \text{ pH} \quad (10)$$

If f approaches zero, Eq. (8) turns to the form

$$E = E^0 - \frac{RT}{F} \ln \frac{\Theta_H}{1 - \Theta_H} - \frac{RT}{F} 2.30258 \text{ pH} \quad (11)$$

This equation corresponds to the dependence²⁻⁴ for the energetically homogeneous surface.

Thermodynamic Data and Calculation

The isotherm of hydrogen chemisorption on the Pt, Ir, and Rh electrodes was measured by Breiter and Bold^{5,6}. From their measurements of dependence of Θ_H on E , the values

of inhomogeneity coefficient f at 25 °C equal 9.0 for Pt, 3.6 for Ir, and 2.8 for Rh were obtained. The value of inhomogeneity coefficient for platinum is near to value 10, reported in the literature⁹.

From the same measurements of Breiter and Böld, we used for calculating the thermodynamic data of hydrogen chemisorption on platinum electrode, the value of potential $E = 0.129$ V against the standard hydrogen electrode (SHE) at which the surface coverage with chemisorbed hydrogen $\Theta_{\text{H}} = 0.5$ is reached. From Eqs (8) and (9), the value $\mu_{\text{H},0}^0 = -23\,830$ J mol⁻¹ or $E^0 = 0.247$ V (SHE) was obtained. In the same way, the values $\mu_{\text{H},0}^0 = -10\,320$ J mol⁻¹ or $E^0 = 0.107$ V (SHE) for the Ir electrode and $\mu_{\text{H},0}^0 = -9\,650$ J mol⁻¹ or $E^0 = 0.100$ V (SHE) for the Rh electrode.

All the other thermodynamic data used for the compounds of Pt, Ir and Rh are summarized in Table I. The oxides presented in Table I are in the literature considered to be hydrated oxides.

TABLE I
Standard Gibbs free energy of water and compounds of Pt, Ir, and Rh at 25 °C

Species	ΔG_{299}^0 , kJ mol ⁻¹	Ref.
PtO(s)	-48.19	1
PtO ₂ (s)	-83.74	1
PtO ₃ (s)	-66.99	1
Pt ²⁺ (aq)	185.77	2
Pt(OH) ₂ (s)	-285.55	1, 10
IrO ₃ (s)	-175.85	1
IrO ₂ (s)	-117.23	1, 10
Ir ³⁺ (aq)	334.94	1
IrO ₄ ²⁻ (aq)	-196.78	1
Rh ₂ O(s)	-83.68	1
RhO(s)	-75.31	1
Rh ₂ O ₃ (s)	-219.66	1
RhO ₂ (s)	-62.76	1
Rh ⁺ (aq)	58.58	1
Rh ²⁺ (aq)	117.15	1
Rh ³⁺ (aq)	230.12	1
RhO ₄ ²⁻ (aq)	-62.76	1
H ₂ O(l)	-237.18	2

The calculation of the potential–pH diagram for three-dimensional compounds was carried out by the procedure given formerly¹. The computation was carried out for the temperature of 25 °C, the activity of ions was considered to be 10^{-6} . For calculating the dependence of potential E (SHE) on pH for the given surface coverage with chemisorbed hydrogen Θ_H , Eq. (8) was used with the above-mentioned values of f and E^0 for single electrodes. The potential–pH diagrams calculated in this way for Pt, Ir and Rh are illustrated in Figs 1 – 3.

The commonly presented curves for hydrogen evolution are not illustrated here because they nearly merge into the dependences of E on pH for $\Theta_H = 0.9$. In all three

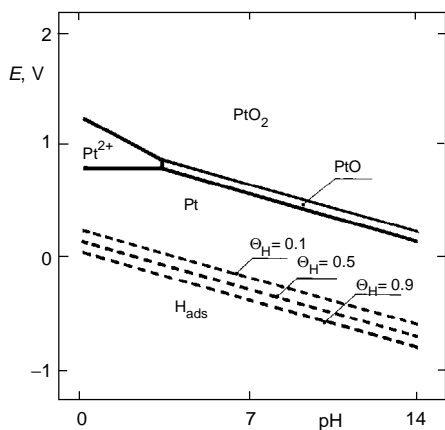


FIG. 1

Potential–pH diagram for Pt–H₂O system at 25 °C

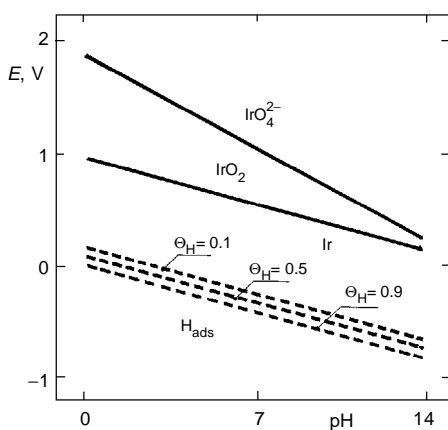


FIG. 2

Potential–pH diagram for Ir–H₂O system at 25 °C

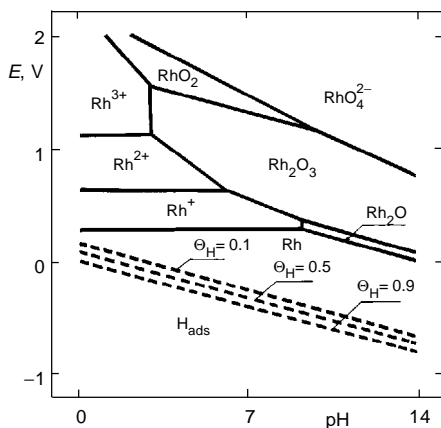


FIG. 3

Potential–pH diagram for Rh–H₂O system at 25 °C

cases the hydrogen chemisorption takes place in the stability domain of metals. The curves for $\Theta_{\text{H}} = 0.1$ and $\Theta_{\text{H}} = 0.9$ are in case of platinum mutually more distant than in case of Ir or Rh. It is caused by a higher inhomogeneity coefficient for platinum than for Ir and Rh.

If we use the simplified Eq. (10) instead of Eq. (8), the curve of the dependence of E on pH for $\Theta_{\text{H}} = 0.1$ is, e.g., for the platinum electrode shifted by 13 mV to more negative values of potentials, for the Ir electrode by 44 mV and for the Rh electrode by 34 mV.

From the potential–pH diagrams expressing the chemisorption on platinum metals, at present is reported only the diagram of chemisorbed sulfur on platinum². In this diagram, the region of chemisorbed sulfur is limited from the side of anodic potentials by the oxidation on sulfate ions. For instance, at pH 1 the oxidation of chemisorbed sulfur is taking place from 90% at the potential 0.403 V (SHE). From the side of cathodic potentials, the region of chemisorbed sulfur is determined by the reduction on $\text{H}_2\text{S}(\text{aq})$ or $\text{HS}^-(\text{aq})$ ions. For instance, the reduction at pH 1 is taking place from 90% at the potential -0.335 V (SHE). In comparison with the diagram given in this work, it is evident that the stability domain of chemisorbed sulfur at more negative values of potentials merges into the stability domain of chemisorbed hydrogen. For a more accurate computation of stability domain of chemisorbed sulfur on platinum electrodes, it is therefore necessary to include also the hydrogen chemisorption into calculation.

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