THE POTENTIAL–pH DIAGRAM DEPICTING THE CHEMISORPTION OF TWO SPECIES ON THE UNIFORMLY INHOMOGENEOUS SURFACE. THE SULFUR AND HYDROGEN CHEMISORPTION ON THE PLATINUM ELECTRODE

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General thermodynamic dependences were derived for the simultaneous chemisorption of two substances on the uniformly inhomogeneous surface. In terms of these dependences and on the basis of thermodynamic data available in the literature, the potential–pH diagram was calculated for the Pt–S–H_2O system at 25 °C on considering the sulfur and hydrogen chemisorption.

The possibility was shown in the papers by Marcus and Protopopoff[1–3] of calculating the potential–pH diagrams depicting the thermodynamic stability domains not only of the three-dimensional but also chemisorbed species. In the preceding paper[4], such a possibility was extended even for the electrode surfaces which are uniformly inhomogeneous, and the computation was carried out of the potential–pH diagrams for the Pt–H_2O, Ir–H_2O, and Rh–H_2O depicting the stability domain of chemisorbed hydrogen. It was shown that the stability domain of chemisorbed hydrogen on the platinum electrode overlapped with a part of stability domain of chemisorbed sulfur[4] which was calculated by Marcus and Protopopoff[1].

The aim of this work is to calculate the potential–pH diagram depicting the simultaneous chemisorption of two species on the surface which is uniformly inhomogeneous. The calculation was carried out for the case of simultaneous chemisorption of sulfur and hydrogen on a platinum electrode.

THEORETICAL

In case of simultaneous chemisorption of species A and B on the surface uniformly inhomogeneous, the dividing of the surface on elements ds is assumed which are so small that the chemisorption takes place on them such as on the surface homogeneous. The chemisorption on the element ds conforms to the relation

$$\mu_{A,s} = \mu_{A,s}^0 + RT \ln \frac{\Theta_{A,s}}{1 - \Theta_{A,s} - \Theta_{B,s}} \ , \tag{1}$$

where $\Theta_{A,s}$ and $\Theta_{B,s}$ are the relative coverages of element ds with species A and B, respectively, $\mu_{A,s}$ and $\mu_{A,s}^0$ are the chemical potential and standard chemical potential, respectively, of the chemisorbed species A on element ds. For the uniformly inhomogeneous surface we have

$$\mu_{A,s}^0 = \mu_{A,0}^0 + (\mu_{A,1}^0 - \mu_{A,0}^0)s \ , \tag{2}$$

where s changes from 0 to 1 and $\mu_{A,0}^0$ and $\mu_{A,1}^0$ stand for the standard chemical potentials of chemisorbed species A on element ds with the highest adsorptivity ($s = 0$) and lowest adsorptivity ($s = 1$), respectively.

Analogous equations, however, with subscript B, hold for species B.

An inhomogeneity coefficient of species A and/or B is defined by the following relation, both the inhomogeneity coefficients being assumed to be the same, i.e.

$$\frac{\mu_{A,1}^0 - \mu_{A,0}^0}{RT} = \frac{\mu_{B,1}^0 - \mu_{B,0}^0}{RT} = f \ . \tag{3}$$

On the basis of the condition of equality of chemical potentials in equilibrium, it is possible to derive the relation

$$\exp\left(\frac{\mu_{A,0}^0 - \mu_{B,0}^0}{RT}\right) = \frac{\Theta_{B,s}}{\Theta_{A,s}} = \frac{\Theta_B}{\Theta_A} = k \ , \tag{4}$$

where Θ_A and Θ_B are the relative coverages of the entire surface with species A and B, respectively. It folows from Eq. (4) that the ratio of relative coverages with both the species is the same on all elements ds and consequently is also equal to the ratio of relative coverages of both the species related to the entire surface.

The total surface coverage with species A is obtained by integration on using Eqs (1)–(4)

$$\Theta_A = \int_0^1 \Theta_{A,s} \, ds = \frac{1}{(1+k)f} \ \ln \frac{1 + (1+k)\,\beta}{1 + (1+k)\,\beta \exp(-f)} \ , \tag{5}$$

where

$$\beta = \exp \frac{\mu_{A,s} - \mu_{A,0}^0}{RT} = \exp \frac{\mu_A - \mu_{A,0}^0}{RT} \ . \tag{6}$$

If k approaches zero, Eq. (5) turns to the form

$$\Theta_A = \frac{1}{f} \ln \frac{1 + \beta}{1 + \beta \exp(-f)} \ ,$$

(7)

which is the equation corresponding to the chemisorption of species A alone on the uniformly inhomogeneous surface[4]. If $k \gg 1$, the value of Θ_A approaches zero.

In the same way it is possible to derive the equation

$$\Theta_B = \frac{1}{(1 + k^{-1})f} \ \ln \frac{1 + \beta'(1 + k^{-1})}{1 + (1 + k^{-1})\beta' \exp(-f)} \ ,$$

(8)

where

$$\beta' = \exp \frac{\mu_{B,s} - \mu_{B,0}^0}{RT} = \exp \frac{\mu_B - \mu_{B,0}^0}{RT} \ .$$

(9)

From Eq. (5) or (8) it is possible to derive the relation

$$\mu_A = \mu_{A,0}^0 + RT \ln \frac{\exp[(\Theta_A + \Theta_B)f] - 1}{(1 + k)\{1 - \exp(-f)\exp[f(\Theta_A + \Theta_B)]\}}$$

(10)

or

$$\mu_B = \mu_{B,0}^0 + RT \ln \frac{\exp[(\Theta_A + \Theta_B)f] - 1}{(1 + k^{-1})\{1 - \exp(-f)\exp[f(\Theta_A + \Theta_B)]\}} \ .$$

(11)

If $k \ll 1$, Θ_B approaches zero and Eq. (10) turns to the form

$$\mu_A = \mu_{A,0}^0 + RT \ln \frac{\exp(f\Theta_A) - 1}{1 - \exp(-f)\exp(f\Theta_A)}$$

(12)

which is the equation corresponding to the dependence of chemical potential of chemisorbed species on the relative surface coverage for the case of chemisorption of one species[4].

CALCULATIONS AND RESULTS

The thermodynamic data of chemisorbed hydrogen on the platinum electrode were taken over from our preceding paper[4]. According to that work, the standard chemical potential of chemisorbed hydrogen on the surface with the highest adsorptivity $\mu_{H,0}^0 = -23\ 830$ J mol^{-1}.

The thermodynamic data of chemisorbed sulfur on platinum were taken over from the work by Marcus and Protopopoff[1] which gives the value of standard chemical potential of chemisorbed sulfur at half-coverage of the platinum surface -103 kJ mol^{-1}. In terms of Eq. (*12*), the value $\mu_{S,0}^0 = -114\ 150$ J mol^{-1} was calculated. The value of inhomogeneity coefficient was assumed to be 9 (ref.[4]).

The other thermodynamic data were taken over from the literature and are summarized in Table I.

The resultant potential–pH diagram for the S–H$_2$O system was calculated in terms of the equations which are summarized in Table II. For the Pt–S–H$_2$O system, the equations were considered which are summarized in Table III.

The stability domains of chemisorbed hydrogen and chemisorbed sulfur were calculated in terms of the following reactions and equations (a_i denotes activity of species i).
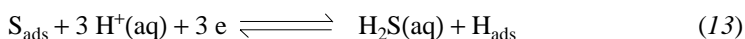
$$S_{ads} + 3\ H^+(aq) + 3\ e \rightleftharpoons H_2S(aq) + H_{ads} \qquad (13)$$

TABLE I
Standard Gibbs free energy of formation of water, platinum and sulfur compounds at 25 °C

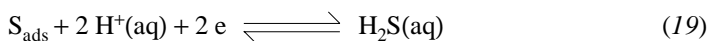| Species	ΔG_{298}^0, kJ mol^{-1}	Ref.
Pt^{2+}(aq)	185.77	1
PtO$_2$(s)	−83.74	5
PtO(s)	−48.19	5
PtS(s)	−77.684	1
PtS$_2$(s)	−101.211	1
H$_2$S(aq)	−27.865	1
HS$^-$(aq)	12.05	1
HSO$_4^-$(aq)	−755.965	1
SO$_4^{2-}$(aq)	−744.626	1
H$_2$O(l)	−237.178	1

$$E = -0.2158 - 0.0197 \log a_{H_2S} - 0.0591 \, pH - 0.0197 \log \frac{\Theta_H}{\Theta_S} \qquad (14)$$

$$S_{ads} + 2 \, H^+(aq) + 3 \, e \; \xrightleftharpoons \; HS^-(aq) + H_{ads} \qquad (15)$$

$$E = -0.3537 - 0.0197 \log a_{HS^-} - 0.0394 \, pH - 0.0197 \log \frac{\Theta_H}{\Theta_S} \qquad (16)$$

$$S_{ads} + H^+(aq) + 2 \, e \; \xrightleftharpoons \; HS^-(aq) \qquad (17)$$

$$E = -0.6540 - 0.030 \log a_{HS^-} - 0.030 \, pH + 0.030 \log \frac{\exp(9 \, \Theta_S) - 1}{1 - \exp[-9(1 - \Theta_S)]} \qquad (18)$$
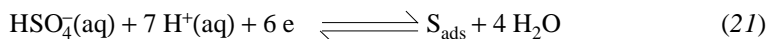
$$S_{ads} + 2 \, H^+(aq) + 2 \, e \; \xrightleftharpoons \; H_2S(aq) \qquad (19)$$

$$E = -0.4471 - 0.030 \log a_{H_2S} - 0.0591 \, pH + 0.030 \log \frac{\exp(9 \, \Theta_S) - 1}{1 - \exp[-9(1 - \Theta_S)]} \qquad (20)$$
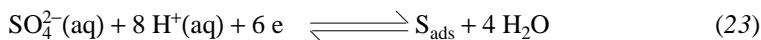
TABLE II
Reactions and corresponding equations for the S–H_2O system at 25 °C, a_i stands for activity of species i

System No.	Reaction/Equation
1	$H_2S(aq) \rightleftharpoons HS^-(aq) + H^+(aq)$ $pH = 6.99 + \log \dfrac{a_{HS^-}}{a_{H_2S}}$
2	$SO_4^{2-}(aq) + 10 \, H^+(aq) + 8 \, e \rightleftharpoons H_2S(aq) + 4 \, H_2O$ $E = 0.301 - 0.00739 \log \dfrac{a_{H_2S}}{a_{SO_4^{2-}}} - 0.0739 \, pH$
3	$HSO_4^-(aq) + 9 \, H^+(aq) + 8 \, e \rightleftharpoons H_2S(aq) + 4 \, H_2O$ $E = 0.2858 - 0.00739 \log \dfrac{a_{H_2S}}{a_{HSO_4^-}} - 0.0665 \, pH$
4	$HSO_4^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H^+(aq)$ $pH = 1.99 + \log \dfrac{a_{SO_4^{2-}}}{a_{HSO_4^-}}$
5	$SO_4^{2-}(aq) + 9 \, H^+(aq) + 8 \, e \rightleftharpoons HS^-(aq) + 4 \, H_2O$ $E = 0.2488 - 0.00739 \log \dfrac{a_{HS^-}}{a_{SO_4^{2-}}} - 0.0665 \, pH$

$$HSO_4^-(aq) + 7\,H^+(aq) + 6\,e \;\rightleftharpoons\; S_{ads} + 4\,H_2O \tag{21}$$

$$E = +0.5276 + 9.85 \cdot 10^{-3} \log a_{HSO_4^-} - 0.0689\,pH +$$
$$+ (-9.85 \cdot 10^{-3}) \log \frac{\exp(9\,\Theta_S) - 1}{1 - \exp[-9(1 - \Theta_S)]} \tag{22}$$

$$SO_4^{2-}(aq) + 8\,H^+(aq) + 6\,e \;\rightleftharpoons\; S_{ads} + 4\,H_2O \tag{23}$$

$$E = +0.5472 + 9.85 \cdot 10^{-3} \log a_{SO_4^{2-}} - 0.0788\,pH +$$
$$+ (-9.85 \cdot 10^{-3}) \log \frac{\exp(9\,\Theta_S) - 1}{1 - \exp[-9(1 - \Theta_S)]} \tag{24}$$

It is apparent from Eqs (14) and (16) for reactions (13) and (15) that in case of simultaneous chemisorption of sulfur and hydrogen, the resulting form of the equation for the dependence of potential on coverage is the same as for the case when the chemisorption takes place according to the Langmuir isotherm.

From the above equations and the equations in Tables II and III, the resultant potential–pH diagram was plotted as it is depicted in Fig. 1. The diagram was constructed for the case when the activity of all ions was $1 \cdot 10^{-6}$. The diagram for the S–H$_2$O and Pt–S–H$_2$O systems which is reported by Marcus and Protopopoff[1] is rather different for it was calculated for the ion activities of sulfur species equal $1 \cdot 10^{-3}$ and for the activity of platinum species equal $1 \cdot 10^{-6}$.

For the comparison of the diagram which for sulfur chemisorbed on platinum was published by Marcus and Protopopoff[1], it is to be summarized: The diagram in this
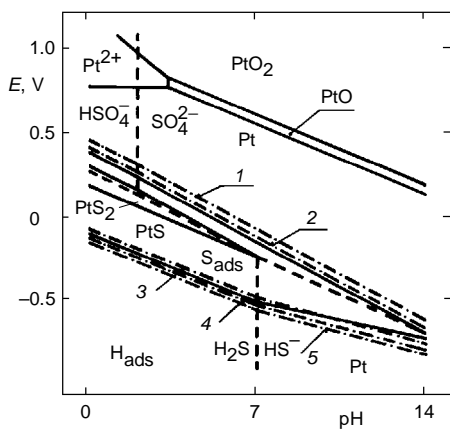

Fig. 1

Potential–pH equilibrium diagram for the Pt–S–H$_2$O system at 25 °C. Activity of ions of sulfur and platinum compounds is $1 \cdot 10^{-6}$. Stability domains of the S–H$_2$O system (– – –), of the Pt–S–H$_2$O system (——) and of the chemisorbed sulfur and chemisorbed hydrogen (– · – · – ·). *1* $\Theta_S = 0.1$, *2* $\Theta_S = 0.9$, *3* $\Theta_H/\Theta_S = 0.01$, *4* $\Theta_H/\Theta_S = 1$, *5* $\Theta_H/\Theta_S = 100$

TABLE III
Reactions and corresponding equations for the Pt–S–H_2O system at 25 °C, a_i stands for activity of species i

System No.	Reaction/Equation
1	$Pt^{2+}(aq) + 2\ e \rightleftharpoons Pt(s)$ $E = 0.9627 + 0.0296 \log a_{Pt^{2+}}$
2	$Pt^{2+}(aq) + H_2O \rightleftharpoons PtO(s)$ $pH = 0.28 - 0.5\ \log a_{Pt^{2+}}$
3	$PtO(s) + 2\ H^+(aq) + 2\ e \rightleftharpoons Pt(s) + H_2O$ $E = 0.9794 - 0.0591\ pH$
4	$PtO_2(s) + 2\ H^+(aq) + 2\ e \rightleftharpoons PtO(s) + H_2O$ $E = 1.0449 - 0.0591\ pH$
5	$PtO_2(s) + 4\ H^+(aq) + 2\ e \rightleftharpoons Pt^{2+}(aq) + 2\ H_2O$ $E = 1.0616 - 0.0296\ \log a_{Pt^{2+}} - 0.1182\ pH$
6	$HSO_4^-(aq) + Pt(s) + 7\ H^+(aq) + 6\ e \rightleftharpoons PtS(s) + 4\ H_2O$ $E = 0.4671 + 9.85 \cdot 10^{-3} \log a_{HSO_4^-} - 0.0689\ pH$
7	$SO_4^{2-}(aq) + Pt(s) + 8\ H^+(aq) + 6\ e \rightleftharpoons PtS(s) + 4\ H_2O$ $E = 0.4867 + 9.85 \cdot 10^{-3} \log a_{SO_4^{2-}} - 0.0788\ pH$
8	$HSO_4^-(aq) + PtS(s) + 7\ H^+(aq) + 6\ e \rightleftharpoons PtS_2(s) + 4\ H_2O$ $E = 0.3736 + 9.85 \cdot 10^{-3} \log a_{HSO_4^-} - 0.0689\ pH$
9	$SO_4^{2-}(aq) + PtS(s) + 8\ H^+(aq) + 6\ e \rightleftharpoons PtS_2(s) + 4\ H_2O$ $E = 0.3932 + 9.85 \cdot 10^{-3} \log a_{SO_4^{2-}} - 0.0788\ pH$
10	$PtS_2(s) + 2\ H^+(aq) + 2\ e \rightleftharpoons PtS(s) + H_2S(aq)$ $E = 0.0225 - 0.0296 \log a_{H_2S} - 0.0591\ pH$
11	$PtS_2(s) + H^+(aq) + 2\ e \rightleftharpoons PtS(s) + HS^-(aq)$ $E = -0.1844 - 0.0296 \log a_{HS^-} - 0.0296\ pH$
12	$PtS(s) + H^+(aq) + 2\ e \rightleftharpoons Pt(s) + HS^-(aq)$ $E = -0.4650 - 0.0296 \log a_{HS^-} - 0.0296\ pH$
13	$PtS(s) + 2\ H^+(aq) + 2\ e \rightleftharpoons Pt(s) + H_2S(aq)$ $E = -0.2582 - 0.0296 \log a_{H_2S} - 0.0591\ pH$

paper includes the stability domain of chemisorbed sulfur and chemisorbed hydrogen and is calculated for the uniformly inhomogeneous surface. The diagram presented in ref.[1] is predetermined for the energetically homogeneous surface and includes only the region of chemisorbed sulfur. The stability domain of chemisorbed sulfur is from the side of anodic potentials in both the works limited by the oxidation on the sulfate or hydrogensulfate anions. Despite use of different adsorption isotherms, both the diagrams differ in this part only slightly. The stability domain of chemisorbed sulfur in the diagram by Marcus and Protopopoff[1] is, on the side of cathodic potentials, limited by the reduction on H_2S(aq). In this work, it is, on the side of cathodic potentials, limited by reactions (*13*) and (*15*) when the chemisorbed sulfur is replaced by chemisorbed hydrogen.

The chemisorption of sulfur on platinum electrodes was investigated in a number of papers[6–10]. Most authors agree on the view that the oxidation of chemisorbed sulfur takes place yielding the sulfate or hydrogensulfate ions, which is in agreement with the two diagrams reported. The oxidation of chemisorbed sulfur, however, according to those works, occurs at more positive potentials than the values calculated on the basis of thermodynamic data. The experimental determinations confirm as well the finding that the presence of chemisorbed sulfur on the surface of platinum electrode makes the hydrogen chemisorption impossible in the hydrogen region (about 0.0 to 0.4 V against the hydrogen electrode in the same solution). The possibility of replacing the chemisorbed sulfur by chemisorbed hydrogen at potentials of hydrogen evolution, however, has not hitherto been observed experimentally.

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