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THERMODYNAMICS OF CHEMISORPTION CONSIDERED AS A PROCESS OF SPECIFIC SURFACE COMPOUNDS FORMATION

The aim of the paper is a proposition of unified thermodynamic treatment of chemisorption, leading to a surface compound formation. It is shown, how the value of the free enthalpy of surface compound formation gives an analogue to "underpotential discharge" in electrochemistry, enabling realization of chemical binding of species on the surface at concentration lower than characteristic for the solubility product of the bulk compound.

Ore processing, e.g., flotation, usually requires an addition of surface active agents or reagents to a slurry consisting of a ground ore suspended in water. Chemical reactions in such systems are usually described with the aid of easily accessible thermodynamic data on bulk phases of the species involved. Since the ground minerals are usually suspended in water delusory information on surface hydrolysis exists with thermodynamic references to hydroxide and oxide bulk phases. Such an approach is often erroneous since in usually very diluted solutions of flotation reagents surface coverages of about one monolayer (or "surface compounds") can exist at concentrations lower than those which are necessary for the formation of the bulk phase of the compounds, even of the same "composition" or rather, stoichiometry.

To prove the above statement let us consider a system containing solid phase of a metal bearing mineral in equilibrium with an aqueous

ERRATA.

do artykułu A. Pomiańskiego i J. Czarneckiego : "Thermodynamics of Chemisorption Considered as a Process of Specific Surface Compounds Formation".

W równaniach (3), (4), (8) i (9) zostały opuszczone znaki Δ (przed G_1 i G_2). W Równaniach (6) i (13) zostały opuszczone symbole ϕ (przed θ) a w równaniach (10) i (11) należy opuścić znaki minus.

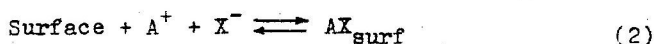
solution of a reagent used, e.g., metal sulphide and aqueous solution of an alkyl xanthate.

Let us consider the following equilibria:

1. formation of a precipitate as a separate bulk phase:



2. chemisorption (surface compound formation) at the mineral - solution interface;



Then the free enthalpies of the above processes can be expressed as:

$$G_1 = \mu_{AX_{\text{prec}}}^0 - \mu_{A^+}^0 - \mu_{X^-}^0 - RT \ln a_{A^+}' a_{X^-}' \quad (3)$$

$$G_2 = \mu_{AX_{\text{surf}}}^0 + RT \ln \Sigma - \mu_{A^+}^0 - \mu_{X^-}^0 - RT \ln a_{A^+}' a_{X^-}' \quad (4)$$

respectively, where $\Sigma = \exp [-(\mu_{AX_{\text{surf}}}^0 - \mu_{AX_{\text{prec}}}^0)/RT]$ is the activity of the "surface phase" AX_{surf} .

Thus, the chemical potential of AX_{surf} can be written as

$$\begin{aligned} \mu_{AX_{\text{surf}}} &= \mu_{AX_{\text{surf}}}^0 + RT \ln \Sigma \\ &= \mu_{AX_{\text{surf}}}^0 + RT \ln \theta + RT \ln \varphi \end{aligned} \quad (5)$$

where θ and φ are surface coverage and surface activity coefficient respectively. The standard chemical potential $\mu_{AX_{\text{surf}}}^0$ may be conveniently defined as the chemical potential of the surface compound at the equilibrium with the bulk AX phase (e.g., with a precipitate). Let this equilibrium occur at the surface excess of Γ_{eq} . Thus, the surface coverage in eq. (5) is

$$\theta = \Gamma / \Gamma_{\text{eq}}, \quad (6)$$

i.e., it is defined as the ratio of the surface excess Γ at the state considered to Γ_{eq} and not to the maximum surface coverage Γ_{∞} . The important point is that precipitation of AX in the bulk may occur at concentrations below those necessary for maximum surface coverage. It is also possible that the maximum surface coverage may be attained below saturation of the bulk solution. Moreover, due to experimental

difficulties in measuring Γ it is not easy to determine accurately the concentration at which the maximum surface coverage is reached. It is thus clear that the state of the maximum surface coverage is ill defined. On the contrary, the state of equilibrium with the bulk phase is well defined and may be, at least in principle, realized experimentally.

The adopted selection of the standard states yields

$$\mu_{AX_{surf}}^0 = \mu_{AX_{prec}}^0 = \mu_{AX}^0 \quad (7)$$

and eqs. (3) and (4) may be rewritten as;

$$G_1 = \mu_{AX}^0 - \mu_{A^+}^0 - \mu_{X^-}^0 - RT \ln a_{A^+}' a_{X^-}' \quad (8)$$

$$G_2 = \mu_{AX}^0 + RT \ln \Sigma - \mu_{A^+}^0 - \mu_{X^-}^0 - RT \ln a_{A^+}' a_{X^-}' \quad (9)$$

The solubility product of the bulk AX precipitate K_{sol} is defined as follows (cf. eq. (8)):

$$- RT \ln K_{sol} = \Delta G_1^0 = \mu_{AX}^0 - \mu_{A^+}^0 - \mu_{X^-}^0 \quad (10)$$

Using the above definition of the solubility product, in the state of equilibrium of the surface compound formation (chemisorption), eq. (9) may be rewritten as:

$$- RT \ln K_{sol} + RT \ln \Sigma - RT \ln a_{A^+}' a_{X^-}' = 0 \quad (11)$$

It must be stressed that the above equation describes surface compound formation only (i.e. reaction (2)), and not its coexistence with the bulk precipitate. The term with K_{sol} was introduced formally to eq. (9) to replace the standard chemical potentials of the species involved. Thus, eq (11) yields:

$$\Sigma = \frac{1}{K_{sol}} a_{A^+}' a_{X^-}' \quad (12)$$

or

$$\theta = \frac{1}{K_{sol}} a_{A^+}' a_{X^-}' \quad (13)$$

Eq. (13) is a general adsorption isotherm. All existing isotherms can be in principle derived from (13) provided the dependence of the surface activity coefficient θ on bulk ion activities is known in an analytical form. It may be also easily written for nonionic substances

or generalized for ionic compounds of other than 1:1 stoichiometry. Eq. (13) is a thermodynamic description of the experimental fact that a solid surface may be covered with chemisorption products or surface compounds even at concentrations at which the bulk solubility product has not been yet exceeded. It has to be noted that the structure and thus the thermodynamic properties of the surface compound may markedly differ from those of the bulk phase of the same chemical individual due to a number of reasons, e.g., to steric restrictions induced by the interface or chemical interactions of the adsorbed molecules with the solid surface alien to the adsorbate. It is thus impossible to assess numerical values of, say Γ_{eq} or Γ_{∞} basing on thermodynamic properties of the bulk precipitate alone. Inspection of eq. (13) clearly shows that some information on surface compound properties (e.g., $\sigma\phi$) are also necessary.

It has to be also pointed out that in mineral dressing one deals with minerals which, even if practically insoluble, may attain a state close to the equilibrium with ions in the solution via surface dissociation or hydrolysis. Thus, additional constraints on ion activities may exist when a flotation reagent is introduced to the system. The exact equations governing these reactions are usually not known. Again it must be stressed that also in that case the compounds undergoing dissociation or hydrolysis must be treated as "surface individuals" with the all resulting conclusions concerning their properties being different from those of the corresponding bulk substances.

STRESZCZENIE

Pomianowski A., Czarnecki J., 1987. Termodynamika procesu chemisorpcji rozumianego jako proces tworzenia specyficznych związków powierzchniowych. Fizykochemiczne Problemy Mineralurgii 19; 83-87.

Celem pracy jest sformułowanie propozycji termodynamicznego opisu chemisorpcji, prowadzącej do powstania związków powierzchniowych.

Pokazano, jak wartość entalpii swobodnej tworzenia związków powierzchniowego określa (w analogii do "podpotencjałowego wydzielania" w elektrochemii), możliwość powierzchniowego wiązania substancji - przy jej stężeniu w układzie nie przekraczającym iloczynu rozpuszczalności, charakterystycznego dla reakcji objętościowej.

СОДЕРЖАНИЕ

А.Помяновски, Я.Чарнацки, 1987. Термодинамика химисорбции, рассматриваемая как процесс образования специфических поверхностных соединений. Физикохимические вопросы обогащения, 19; 83-87.

Целью работы является формулировка предложения термодинамического описания химисорбции, ведущей к образованию поверхностных соединений. Показано, что значение свободной энтальпии образования поверхностного соединения определяет (аналогично "потенциальному выделению" в электрохимии), возможность поверхностной связи вещества при ее концентрации в системе, не преувеличивающей произведения растворимости характеристичного для объемной реакции.