

Theoretical investigation of isopleths of hydrogen solubility in transition metals

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Abstract

The calculation of thermodynamic potential and of equilibrium equations defining the P – T – c diagrams was performed for metals and alloys of arbitrary structure and any composition with an impurity of hydrogen atoms distributed in positions of two types. The character of the functional dependences of isopleths was established. The results of the calculations were compared with experimental isopleths of hydrogen solubility in V, Na, Y, Ti, Zr, Ta, Th, Pu metals and Ti–Zr alloy. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

As is generally known, the solubility of gases (hydrogen, nitrogen, oxygen) in metals and alloys considerably affects their properties. The limiting concentration of gases atoms depends on pressure, P , and temperature, T , to a considerable extent.

The study of P – T – c curves is the fundamental method of investigation of introduction phases. The view of these diagrams depends heavily on the character of distribution of the atoms of gases over positions of different types, on the crystalline structure and on the composition and degree of atomic ordering in alloys. A calculation of isopleths of hydrogen solubility in alkali metals has been made in the present paper.

2. Isopleths of hydrogen solubility

A great number of experimental research papers are available on the investigation of P – c isotherms, T – c isobars and P – T isopleths of the solubility of gases in metals and alloys [1–11]. The CrN, CdN, HfN, NbN, TiN, LiH, NaH, KH, ZrO, TaO, FeO, CoO, NiO phases with B1 structure of NaCl type have been adequately covered. The view of P – T – c plots depends to a great extent on the character of distribution of the atoms of gases over positions of different types, on the crystalline structure and

on the composition and degree of atomic ordering in the case of alloys. The redistribution of the atoms of gases in crystal and phase transitions can modify these plots.

Theoretical investigations of isopleths of hydrogen solubility in metals and alloys of arbitrary structure and any composition are made in the present paper. The possible character of the $\ln P$ dependence as a function of $1/T$ is elucidated and the reasons why this dependence departs from linearity is ascertained.

The calculation of the thermodynamic potential, Φ , by the method of average energies taking into account the pressure dependence of crystal volume, lattice constant, activity of hydrogen atoms and their energies leads to

$$\begin{aligned} \Phi = & N_1 c_1 (u_1 - \alpha_1 P) + N_2 c_2 (u_2 - \alpha_2 P) \\ & + kTN \{ \nu_1 [c_1 \ln c_1 + (1 - c_1) \ln (1 - c_1)] \\ & + \nu_2 [c_2 \ln c_2 + (1 - c_2) \ln (1 - c_2)] \} + PV(1 - \chi P) \\ & - kTND(\nu_1 c_1 + \nu_2 c_2) \ln P \end{aligned} \quad (1)$$

where k is the Boltzmann's constant, N_1 and N_2 are the numbers of positions of two types occupied by hydrogen atoms ($N = N_1 + N_2$), c_i is atomic concentration of hydrogen in position $i = 1, 2$ in relation to the numbers N_i , ν_i is the relative concentration of positions of i -type, u_i is the energy of hydrogen atom in position i at $P=0$, V is the crystal volume at $P=0$, D is the constant factor in the pressure dependence of hydrogen atoms activity, $\chi = -1/V \cdot \partial V / \partial P$ is the crystal compressibility, $\alpha_i = 1/3 \chi d (\partial u_i / \partial d)_{P=0}$, d is the lattice constant. Eq. (1) for the special

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case of one type positions of hydrogen atoms is derived in [12]. The calculation of thermodynamic potential, Φ , is presented in [13] taking account of external uniform pressure, P , and with justification of the linear dependence of hydrogen atoms energies on pressure.

At the state of thermodynamic equilibrium the following conditions are fulfilled

$$\frac{\partial \Phi}{\partial c_1} = 0, \quad \frac{\partial \Phi}{\partial c_2} = 0 \quad (2)$$

The substitution of expression (1) into (2) gives

$$D \ln P = \ln \frac{c_i}{1 - c_i} + \frac{u_i - \alpha_i P}{kT}, \quad i = 1; 2 \quad (3)$$

from which we determine the full atomic concentration

$$c = \nu_1 c_1 + \nu_2 c_2 \quad (4)$$

of hydrogen for $c \ll 1$ with an accuracy of constant factor (with D factor taken as unity) in the following form

$$c = P \left(\nu_1 \exp \frac{-u_1 + \alpha_1 P}{kT} + \nu_2 \exp \frac{-u_2 + \alpha_2 P}{kT} \right) \quad (5)$$

Eq. (5) determines P - T - c curves of hydrogen solubility in metal or alloy for the special case of small filling numbers ($c \ll 1$). For alloys the u_i energy depends on composition and degree of atomic order.

From Eq. (5) it follows that owing to the different positions of hydrogen atoms the $\ln P$ dependence on $1/T$ at concentration $c = \text{const}$ will be not linear even at $\alpha_1 = \alpha_2 = 0$.

On condition that hydrogen atoms occupy the positions of one type ($N_1 = N$, $N_2 = 0$, $u_1 = u$, $\alpha_1 = \alpha$) the calculation of P - T - c curves for all filling numbers ($c \leq 1$) at $D = 1$ gives the following equation

$$\ln P = \ln \frac{c}{1 - c} + \frac{u - \alpha P}{kT} \quad (6)$$

from which it follows that at $\alpha = 0$ isopleths (the $\ln P$ dependence on $1/T$) will be straight lines. In this case $\ln(c/1 - c)$ value defines the isopleths level and the u/k value characterizes its slope. The slope of isopleth is subject to variation owing to the α value and non-linearity may occur.

Fig. 1 gives as an example the plots of isopleths constructed by Eq. (6) for great filling numbers $c = 0.9; 0.95; 0.99$, energy $u = -0.5$ eV and coefficients $\alpha = 0; 0.01; \pm 0.001$. The isopleths are linear and parallel at $\alpha = 0$. If $\alpha \neq 0$, so at $c = 0.9$ the slope of isopleths is changed, in the case $\alpha > 0$ the slope is decreased and in the case $\alpha < 0$ it is increased. With the increase in c concentration the non-linearity of the isopleths is manifested, the curvature of the curve increases as the α coefficient increases, for $\alpha > 0$ the curve convexity is directed from the abscissa axis and for $\alpha < 0$ the convexity is directed toward the x axis.

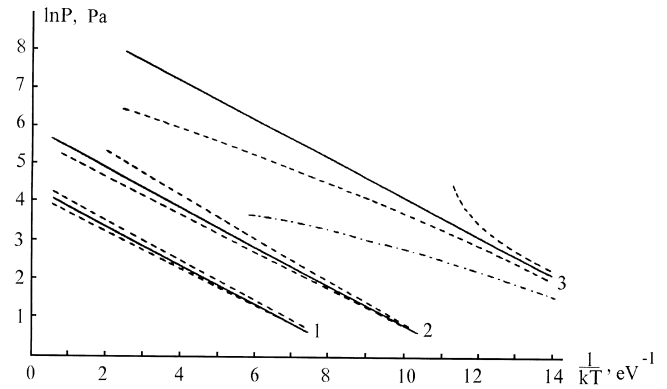


Fig. 1. Theoretical isopleths of hydrogen solubility in metal constructed by Eq. (6) for energy $u = -0.5$ eV, for limiting concentrations $c = 0.9; 0.95; 0.99$ (curves 1, 2 and 3, respectively) and for different coefficients: $\alpha = 0$ (straight lines), $\alpha > 0$ (dotted and dash-dotted curves below the straight lines), $\alpha < 0$ (dotted curves above straight lines). The coefficient α takes the values $\alpha = \pm 0.001$ for the dotted curves and $\alpha = 0.01$ for the dash-dotted curve.

The obtained theoretical results were found to be in complete agreement with experimental data. Fig. 2 shows the experimental isopleths of hydrogen solubility in some metals and in the Ti-Zr alloy [5,14]. One can see all the predicted features of functional dependence of isopleths in these plots. The units of measurement of pressure (mmHg and cmHg) have been retained in the plots and the natural or decimal logarithm remain unchanged according to the papers from which they are adopted. Fig. 2 shows that isopleths are linear for vanadium, sodium and yttrium; apparently α coefficients tend towards zero ($\alpha \rightarrow 0$) for these metals. For all this, for Na and Y the isopleths slope is changed with the increasing concentration of hydrogen. This is the result of a change in the crystalline structure at α the phase transition, i.e. owing to the different u energies of different phases. Moreover, the isopleths coincide in the case of concentration of NaH phase over the interval 0.3–0.8. This corresponds to the conservation of hydrogen solubility limit in the phase, the amount of which is increased. For the Ti-H phases the $\alpha \rightarrow \beta$ phase transition takes place in the region of temperature measurement. At the phase transition the distinguishing features appear on the isopleths in the form of a curve (coexistence of α and β phases). In addition, the isopleths level is raised with the increase of hydrogen concentration. For α and β phases the slopes of the isopleths are different, suggesting that value of the u energies of the α and β phases differ. For tantalum, thorium, plutonium, zirconium and the Ti-Zr alloy the isopleths are curvilinear. This means that the α value influences the isopleth plots. From the plots of the isopleths it can be assumed that the α value is negative for the Ta, Th and Zr metals and the Ti-Zr alloy, and it is positive for the Pu metal. Furthermore, the phase transformations are observed in the region of hydrogen concentration as 1–1.3 for Zr-H, 0.5–1 for Th-H and 0.5–1.5

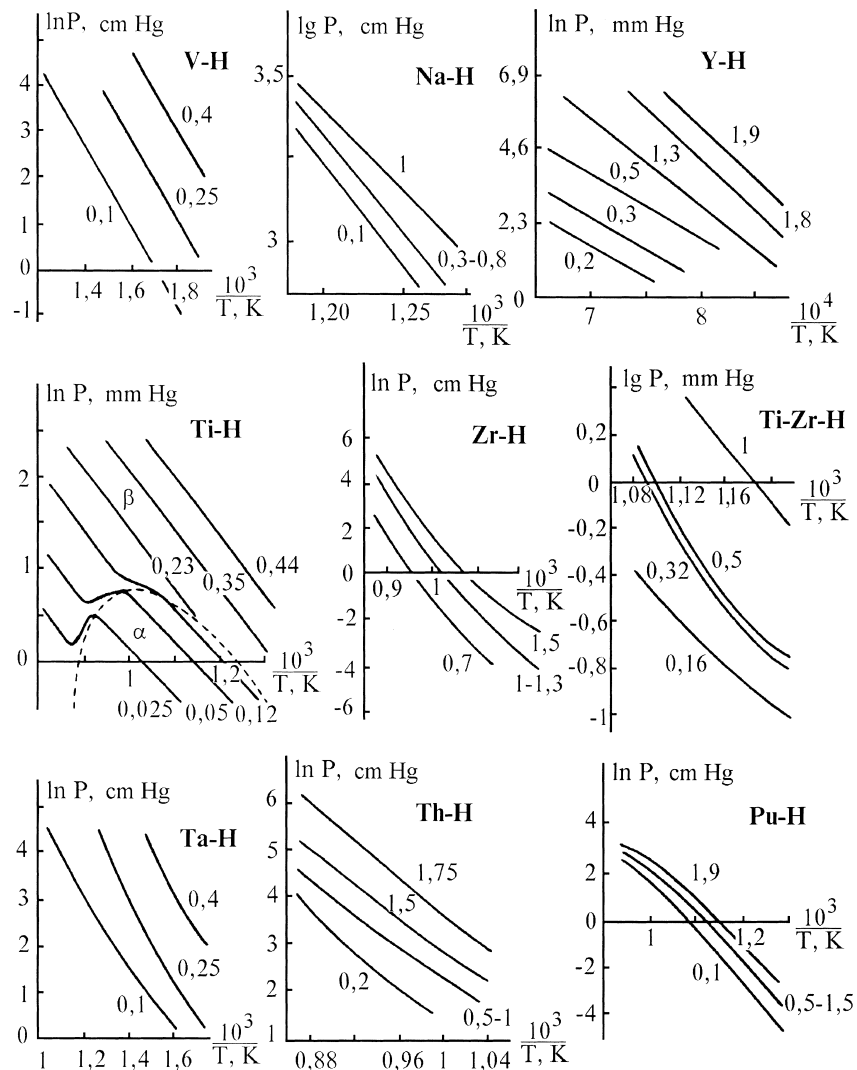


Fig. 2. Experimental isopleths of hydrogen solubility in metal–hydrogen systems. Number close by curves point out the relative atomic concentration H:Me (the content of NaH phase for the Na–H system). The dotted line indicates the boundary between α - and β -phases for the Ti–H system [5,14].

for Pu–H and the isopleths coincide over these concentration intervals.

3. Conclusions

By the use of the obtained Eq. (6) the experimental study of isopleths enables estimation from the plots of the energetic parameter u and the coefficient α for each concrete system and its phases, to find out the phase transitions and to evaluate their concentration range. Comparing Eq. (5) with experimental isopleths one can clarify whether or not the hydrogen atoms are distributed in positions of different types. The obtained theoretical results and the receipt of all this information are of scientific interest to engineers.

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