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Modelling of phase equilibria in metal–hydrogen systems

M.V. Lototsky[a,b], V.A. Yartys[a,*], V.S. Marinin[b], N.M. Lototsky[c]

[a] *Institute for Energy Technology, P.O. Box 40, N-2027 Kjeller, Norway*
[b] *Institute of Mechanical Engineering Problems of the National Academy of Sciences, Kharkiv 61046, Ukraine*
[c] *Kharkiv National University, Kharkiv 61108, Ukraine*

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Abstract

The paper presents a model quantitatively describing phase equilibria in metal–hydrogen systems. It is based on a formal consideration of interstitial hydrogen dissolved in the metal matrix as a van der Waals lattice gas. The model describes the asymmetry of the experimental 'pressure–composition' isotherms. It postulates an existence of local fluctuations in the stoichiometric composition of the alloys, causing an appearance of statistical deviations of the correlated values of entropy and enthalpy from their corresponding mean values. The model describes temperature-dependent plateau slopes and smooth transitions between α-, (α+β)- and β-regions. It was applied in the approximations of both single ($LaNi_{4.8}Sn_{0.2}$–H_2) and double plateau ($TiCr_{1.9}$–H_2) experimental PCT-diagrams.

Keywords: Hydrogen storage materials; Thermodynamics; PCT diagram; Modelling

1. Introduction

Modelling of phase equilibria (PCT diagrams) in the systems of hydrogen gas with hydride forming metals and alloys is important both for the systemic evaluation of the available experimental data and for the optimisation of specific applications of metal hydrides.

Lacher-type models [1–3] are the most frequently applied to describe the PCT diagrams. A linear decrease of the enthalpy contribution, $\bar{H}(\theta)$, into an excessive (in comparison with the ideal lattice gas) chemical potential of intersitital hydrogen dissolved in the metal matrix, is postulated with the rise of H content:

$$\bar{H}(\theta) = \bar{H}_0 + E_{HH}(\theta); \quad E_{HH}(\theta) = -h \cdot \theta; \quad h > 0 \tag{1}$$

Here $\theta = C/C_{max}$ is the filling fraction; C and C_{max} are current and limiting hydrogen concentrations respectively; $E_{HH}(\theta)$ is the energy of indirect H–H interaction; $\bar{H}_0$ and h are constants. The following equation describes the sorption isotherm in this case:

$$\ln P = \ln P_0 + 2\ln\left(\frac{\theta}{1-\theta}\right) - 8\frac{T_c}{T}\theta \tag{2}$$

Here $T_c = h/4R$ is the critical temperature, P is the equilibrium hydrogen pressure, and P_0 is the concentration independent contribution to its value. P_0 is determined as:

$$\ln P_0 = -\frac{\Delta S_0}{R} + \frac{\Delta H_0}{RT} \tag{3}$$

where ΔS_0 and ΔH_0 are the entropy and enthalpy contributions, and R is the gas constant.

At temperatures below T_c model isotherms acquire a form of loop-like curves. Such a behaviour is interpreted as a phase transition at constant pressure, where θ undergoes discontinuous increase from θ_α to θ_β and a plateau appears.

In Ref. [2] the Lacher model has been extended to the consideration of the multi-plateau isotherms. The model isotherm is obtained by a superposition of several, depending on the experimentally observed number of plateaux, single-segment isotherms:

$$C = C_{max}\sum_{i=1}^{m} g_i\theta_i(P) \tag{4}$$

Here m is the number of plateaux, g_i is the fraction of the i-th plateau segment, and θ_i is calculated for each plateau segment from Eqs. (2) and (3).

A characteristic feature of Lacher-type isotherms is their antisymmetry in the coordinates $\theta - \ln P$ with a midpoint $\theta_0 = 1/2$ [2,3]. The Lacher isotherm describes a simplified, ideal rather than real behaviour of the metal–hydrogen systems. The experimental isotherms are usually asymmet-

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*Corresponding author. Tel.: +47-63-806-453; fax: +47-63-810-920.
E-mail address: volodymyr.yartys@ife.no (V.A. Yartys).

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ric, so the filling fraction θ_0 in the plateau midpoint (or in the inflection point of the isotherm above the critical temperature) is usually smaller than 1/2. Furthermore, in most cases, on a transition from a single phase to the two-phase region, the pressure–concentration dependence is smooth, and the plateau has a pronounced slope. This problem was considered in [4] where a Gaussian distribution of the plateau pressures was suggested in modelling the isotherms with a plateau slope. To take into account the asymmetry of the isotherm, separate fitting parameters for α and β phases were introduced, with 15 parameters used to describe a single plateau PCT dependence. The temperature dependence of the plateau slope has not been considered in [4].

The aim of this work was to develop a simple model and a corresponding PC software to describe and simulate PCT diagrams, which will take into account the experimentally observed non-ideal behaviour of the metal hydride systems.

2. Modelling of asymmetric isotherm

General description of the metal–hydrogen (M–H) PCT diagrams should include consideration of both M–H and H–H interactions. As an approximation, hydrogen subsystem can be treated separately from the metal matrix [5]. Considering only attractive and indirect H–H interactions, mediated via the metal atoms, gives the dependencies presented in Lacher-type Eqs. (1) and (2) [3,6]. H–H repulsion is an additional characteristic feature for interstitial H in the metal hydrides, especially at high H/M ratios [7]. Such interactions are not accounted for by Lacher-type models.

The simplest approach, taking into account both attractive and repulsive interactions between adsorbate molecules in a condensed phase, is a consideration of the latter as a van der Waals gas. The monomolecular surface adsorption based on the latter model of interaction of the molecules of adsorbate was considered by Hill–de Boer [8]. Their consideration was limited to non-dissociative gases. Applying the model of Hill–de Boer to hydrogen as a lattice gas and extending the model by accounting for H_2 dissociation, the following expression is derived:

$$\ln P = \ln P_0 + 2\ln\left(\frac{\theta}{1-\theta}\right) - \frac{27}{2}\frac{T_c}{T}\theta + 2\frac{\theta}{1-\theta} \tag{5}$$

The differences in the PCT diagrams for the Lacher model (Eq. (2)) and for the modified equation of Hill–de Boer (Eq. (5)) are clearly seen from the isotherms presented in Fig. 1. In contrast to the Lacher model, the proposed model provides narrowing of the isotherms along the θ axis and exhibits their asymmetry. The evaluation of the position of the plateau is more complicated compared to the Lacher model. The value of θ_{0V} corresponding to the plateau midpoint depends on the temperature covering a range from 1/3 ($T=T_c$) to 1/2 ($T=0$). The relation between the values of ΔS_0 and ΔH_0 in Eq. (3) and observed standard entropy and enthalpy ($\Delta S°$ and $\Delta H°$) calculated from van't Hoff dependencies of plateau pressure versus temperature are expressed as:

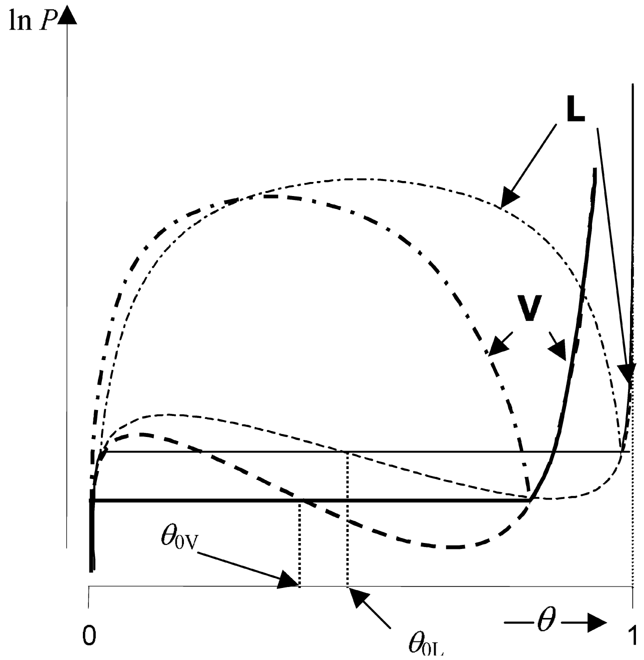


Fig. 1. Calculated pressure–composition isotherms ($T=1/2T_c$) for the Lacher model (L; plateau midpoint at $\theta_{0L}=1/2$) and the model of van der Waals lattice gas (V; plateau midpoint $\theta_{0V}<1/2$). Note that both isotherms have the same vertical asymptote $\theta=1$, but van der Waals dependence approaches this value at significantly higher pressures.

$$\begin{aligned}\Delta H° &= \Delta H_0 - \frac{27}{2}RT_c\theta_{0V}\\ \Delta S° &= \Delta S_0 - 2R\left(\ln\frac{\theta_{0V}}{1-\theta_{0V}} + \frac{\theta_{0V}}{1-\theta_{0V}}\right)\end{aligned} \tag{6}$$

The proposed consideration of interstitial hydrogen as a van der Waals gas is a *formal* approach. Since H atoms in solids are not freely mobile and confined to the specific occupied interstitial positions, it does not describe a particular mechanism of the interaction. However, as it will be shown later in the present paper, this model allows to improve the fitting of the experimental PCT data compared to the Lacher model, especially for the non ideal isotherms.

3. Non-ideality of the pressure–composition isotherms

The approach for the modelling of multi-plateau isotherms [2] can be extended to consider non-ideal isotherms in the real systems (smoothening of phase transitions and existence of temperature-dependent plateau slopes) [9].

The latter features can be explained by appearance of the local fluctuations of the stoichiometric composition of the alloys [10]. This, in turn, causes a modulation of P_0 (Eq. (3)), which is a characteristic constant of a specific material. When the fluctuations in the chemical composition will be infinitesimal, a discrete partition on fractions, g_i, can be substituted by a continuous distribution function, $\varphi(u)$. Then Eq. (4) has to be modified to introduce a convolution of the $\theta(u)$ function on the argument's partition density $\varphi(u)$. Assuming as a fluctuating parameter $X = \ln[P(\theta)] - \ln[P(\theta_{0\mathrm{V}})]$, where $\theta_{0\mathrm{V}}$ corresponds to the midpoint of the plateau, gives

$$C = C_{\max}\int_{a}^{b}\theta(X)\varphi(X-u)\,\mathrm{d}u \qquad (7)$$

If the Gaussian distribution law is postulated, then the isotherm equation can be written as

$$\theta = \frac{C}{C_{\max}} = \frac{1}{\sigma\sqrt{2\pi}}\int_{-\infty}^{+\infty}\theta(X)\exp\left[-\frac{(X-u)^2}{2\sigma^2}\right]\mathrm{d}u \qquad (8)$$

where $\theta(X)$ should be calculated from the phase equilibria model (Eq. (5)) and σ is a standard deviation of the X (or $\ln P_0$) value.

Fig. 2 illustrates Eq. (8), where the starting model isotherm is convoluted on a Gaussian distribution function. The procedure is similar to the one described in [4], however, we consider the asymmetric isotherm in total, including both single- and two-phase regions. Such a consideration simplifies the model reducing significantly the number of fitting parameters compared to [4].

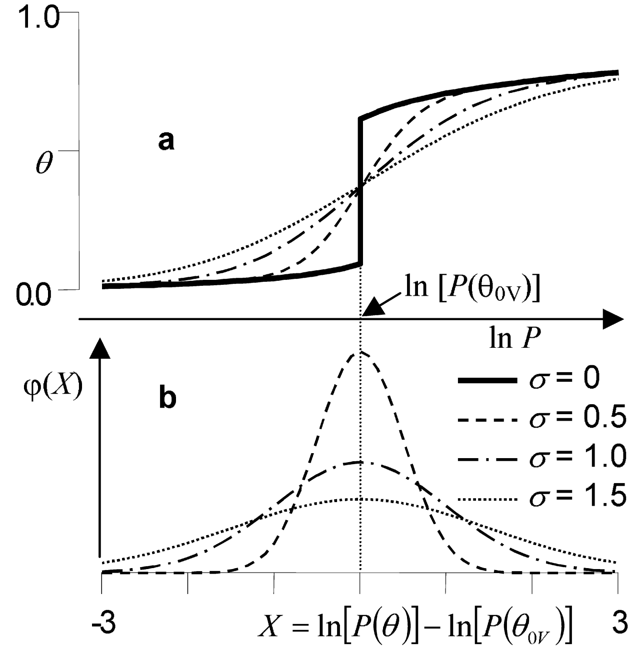


Fig. 2. (a) The 'ideal' model isotherm at $T=5/6T_c$ built with use of Eq. (5) (solid line; $\sigma=0$) and the isotherms resulting from its convolution according to the Eq. (8) (dashed and dotted lines; $\sigma=0.5$, 1.0, 1.5); (b) corresponding Gaussian distribution functions.

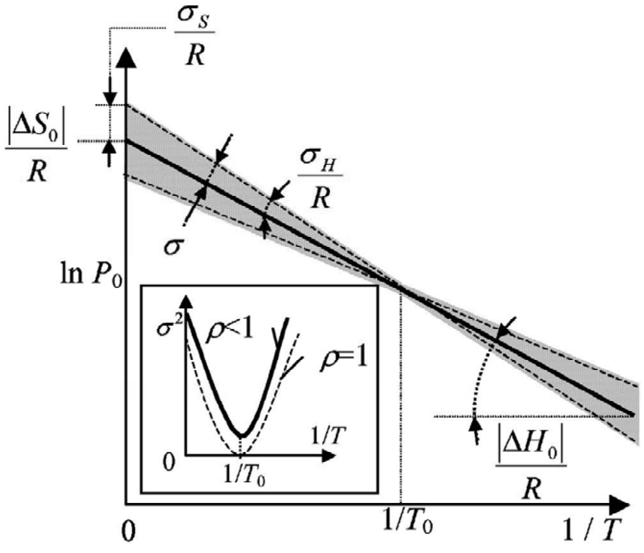


Fig. 3. Temperature dependence of P_0 and its deviations.

Since the fluctuations of $\ln P_0$ are caused by the fluctuations of ΔS_0 and ΔH_0, then, taking into account Eq. (3), the deviation σ can be expressed through corresponding deviations of these values, σ_S and σ_H, as follows

$$\sigma^2 = \frac{\sigma_S^2}{R^2} + \frac{\sigma_H^2}{R^2T^2} - \frac{2\rho_{SH}\sigma_S\sigma_H}{R^2T}, \qquad (9)$$

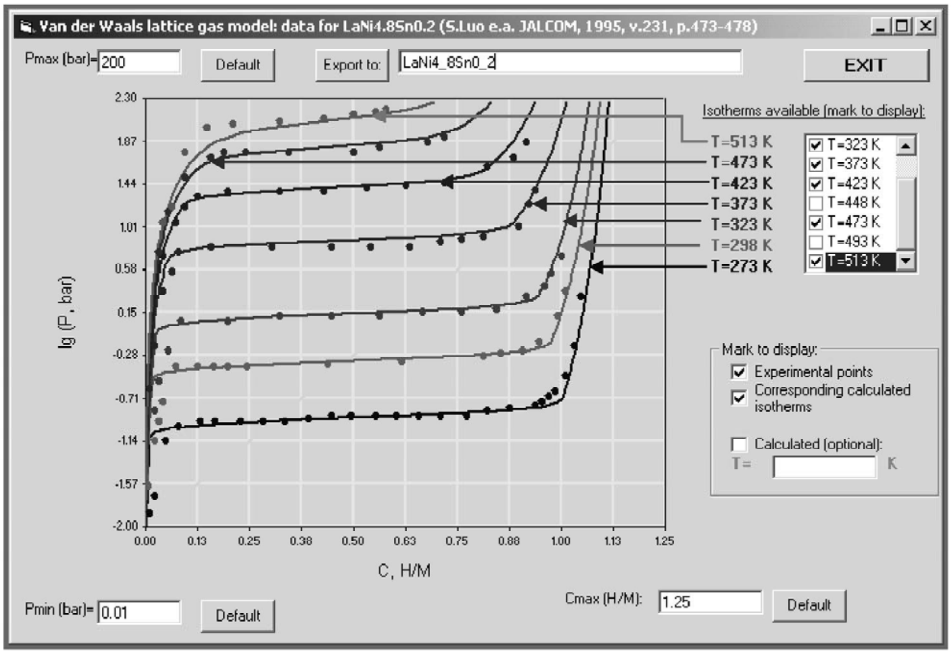
where ρ_{SH} is a correlation coefficient between ΔS_0 and ΔH_0.

Eq. (9) gives the temperature dependence of the deviations of the real 'pressure–composition' isotherms from their ideal behaviour, including plateau slope. According to [10], the value of plateau slope, $\partial \ln P_i/\partial C$, is linearly dependent from the reciprocal temperature passing zero at some temperature T_0. From Eq. (9) it follows that σ (which is proportional to the plateau slope in the midpoint) has a minimum at $T_0 = \sigma_H/\sigma_S$ (Fig. 3). Complete correlation, $\rho_{SH}=1$, converts the model to the ideal case, $\sigma(T_0)=0$.

4. Approximation of the experimental data

Here we shall consider two examples of the approximation of the experimental data by the proposed model. Fig. 4 illustrates the application to the single plateau system ($\mathrm{LaNi_{4.8}Sn_{0.2}}$–$\mathrm{H_2}$), and Fig. 5 presents the case of the double plateau system $\mathrm{TiCr_{1.9}}$–$\mathrm{H_2}$. The procedure of modelling multiplateau isotherms is similar to Kierstead [2]. The fractions g_i for each plateau segment (Eq. (4)) are introduced in our model as fitting parameters.

Figs. 4 and 5 represent user interface of the authors'



Van der Waals lattice gas model: data for LaNi4.8Sn0.2 (S.Luo e.a. JALCOM, 1995, v.231, p.473-478)

Pmax (bar)= 200

Export to: LaNi4_8Sn0_2

Isotherms available (mark to display):
☑ T=323 K
☑ T=373 K
☑ T=423 K
☐ T=448 K
☑ T=473 K
☐ T=493 K
☑ T=513 K

Mark to display:
☑ Experimental points
☑ Corresponding calculated isotherms
☐ Calculated (optional): T= K

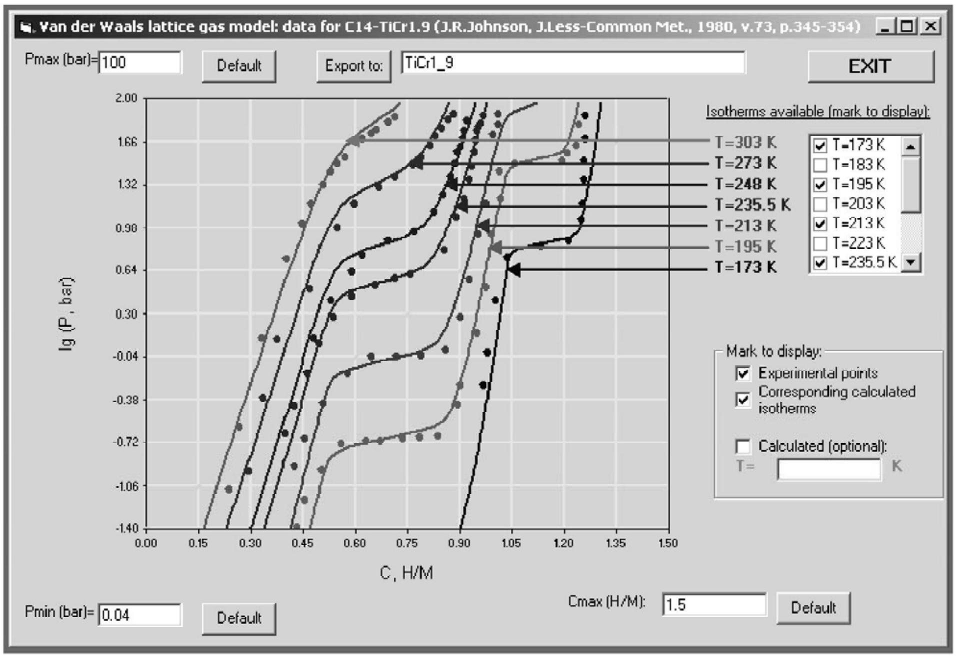
Pmin (bar)= 0.01

Cmax (H/M): 1.25

Fig. 4. Approximation of the PCT diagram for the system $LaNi_{4.8}Sn_{0.2}$–H_2 at $T=273$–513 K [11]: $C_{max}=1.26$ H/M; $T_c=491.8$ K; $\Delta H_0=-11.16$ kJ/mole H_2; $\Delta S_0=-100.37$ J/(mol $H_2\cdot$K); $\sigma_H=520$ J/mole H_2; $\sigma_S=1.84$ J/(mole $H_2\cdot$K); $\rho_{SH}=0.77$.

(MVL) software realising the described model. The fitting parameters are presented in the figure captions.

Application of the proposed model allows to approximate rather complex experimental data. An average error in the calculation of the hydrogen concentration does not exceed 0.03 H/M. Comparison of the experimentally observed (i.e. derived from the van't Hoff plots) enthalpy and entropy of hydrogenation with corresponding calculated values (Eq. (6)) shows a reasonably good agreement (Table 1). The most significant discrepancies take place for



Van der Waals lattice gas model: data for C14-TiCr1.9 (J.R.Johnson, J.Less-Common Met., 1980, v.73, p.345-354)

Pmax (bar)= 100

Export to: TiCr1_9

Isotherms available (mark to display):
☑ T=173 K
☐ T=183 K
☑ T=195 K
☐ T=203 K
☑ T=213 K
☐ T=223 K
☑ T=235.5 K

Mark to display:
☑ Experimental points
☑ Corresponding calculated isotherms
☐ Calculated (optional): T= K

Pmin (bar)= 0.04

Cmax (H/M): 1.5

Fig. 5. Approximation of the PCT diagram for the system C14–$TiCr_{1.9}$–H_2 at $T=173$–303 K [12]: $C_{max}=1.54$ H/M; $g_0=0.46$. Plateau #1 ($g_1=0.34$): $T_c=249.5$ K; $\Delta H_0=-16.41$ kJ/mole H_2; $\Delta S_0=-123.18$ J/(mole $H_2\cdot$K); $\sigma_H=347$ J/mole H_2; $\sigma_S=1.43$ J/(mole $H_2\cdot$K); $\rho_{SH}=0.59$. Plateau #2 ($g_2=0.20$): $T_c=220.0$ K; $\Delta H_0=-10.02$ kJ/mole H_2; $\Delta S_0=-126.13$ J/(mole $H_2\cdot$K); $\sigma_H=286$ J/mole H_2; $\sigma_S=0.89$ J/(mole $H_2\cdot$K); $\rho_{SH}=0.89$.

Table 1
Calculated and experimental values of thermodynamic parameters

Parameter	$LaNi_{4.8}Sn_{0.2}$ (Fig. 4)		C14–$TiCr_{1.9}$ (Fig. 5)			
	Calculated	Experimental [11]	Plateau ≠ 1		Plateau ≠ 2	
			Calculated	Experimental [12]	Calculated	Experimental [12]
$\Delta H°$ (kJ/mole H_2)	−33.2	−32.8	−26.2	−26.2	–19.9	–19.8
$\Delta S°$ (J/mole $H_2 \cdot K$)	−104.7	−105.0	−121.8	−122.0	–130.5	–130.5
T_c (K)	491.8	≥513	249.5	~290	220.0	~240

the critical temperatures T_c exhibiting negative deviations from the experimental data.

In case of C14–$TiCr_{1.9}$ intermetallic compound the asymptotic behaviour of $\ln(P)$ at small H concentrations corresponds to a nonzero H content in the material, $C = C_{min}$. This phenomenon for the $TiCr_{1.9}$–H system was accounted as resulting from H trapping by the sample [3]. In Ref. [3] the value of C_{min} was obtained by separate low-pressure measurements. We have described the isotherm by introducing an extra, imaginary low-pressure plateau segment (fraction g_0) with a very low critical temperature T_c.

5. Conclusions

In present paper we have proposed the model simulating multiplateau PCT diagrams in the systems of hydrogen gas with hydride forming metals and alloys. The model is based on the formal consideration of interstitial hydrogen as a van der Waals lattice gas. It takes into account the asymmetric behaviour of the real isotherms.

The smoothed transitions between single- and two-phase regions, as well as plateau slope are modelled assuming a random character of correlated values of entropy and enthalpy contributions into the plateau pressure, due to fluctuations of the stoichiometry of the alloy.

Acknowledgements

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