EFFECT OF PRESSURE ON THERMO-DINAMIC PROPERTIES OF METAL HYDRIDES

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The data obtained before by the authors and other researchers [1,2,3] have shown that thermo-dynamic properties of compounds depend on their elastic dynamic characteristics and external factors. This work is devoted to calculation of such dependences for a number of hydrides. We have calculated the following thermo-dynamic functions: enthalpy ($\Delta H^o_{293\,K}$), heat capacity (C^o_p), entropy (S^o), and free energy (Gibbs potential) ($\Delta\Phi^o_{293\,K}$). The calculation techniques included the use of the GO LCAO method for determination of the atomisation energy (E_a,eV/at) of objects under study, followed by a quantitative analysis of their elastic dynamic state in the frame of the one-parameter model of atom-atom interaction energy [2]. Thus, the elastic compression modulus (β, Pa), melting point (T_m, K), Debye temperature (θ_D, K), linear expansion coefficient (α_T, K^{-1}), coefficient of heat conductivity (λ,W/cm·K), and coefficient of heat capacity (C_p,J /mol.K) have been calculated. For normal conditions the following relations have been derived:

$\beta = (z \cdot E_a \cdot 1{,}602 \cdot 10^{-12}) / (27d^3)$;
$T_m = (E_a \cdot 1{,}602 \cdot 10^{-12}) / (41 \cdot k)$;
$\theta_D = 2{,}75 \cdot 10^{6} \cdot (E_a / A)^{0,5} \cdot \hbar / (d \cdot k)$;
$\alpha_T = 3 \cdot k / (z \cdot E_a \cdot 1{,}602 \cdot 10^{-12})$;
$\lambda_{ph} = z^{0,5} \cdot E_a \cdot k \cdot 4.10^{-21} / (d \cdot \hbar)$;
$C_p = (8.3 \cdot 10^{16} \cdot k T^2 / \theta_D^2) \cdot (1.5 - T/\theta_D)$ for $T < \theta_D$.
$\Delta H_T = -E_a + \int C_p\, dT$; $\Delta S_T = \int (C_P/T)\, dT$;
$\Delta\Phi_T = \Delta H_T - T \cdot \Delta S_T$.

Hear E_a is the atomization energy (eV/at), z is the coordination number for the nearest neighbors, d is the averaged interatomic distance in this neighborhood (cm), k=1,38·10^{-16}erg.K^{-1}, $\hbar$ = 1.05·10^{-27} erg.sec (constants of Boltsmann and Planck, respectively), and A is the atomic weight in atomic units.

To take into account pressure and temperature effects, the following relations were used: $\beta(P) = 1 / (1/\beta_0 - k \times P/\beta_0^2)$,

$$\beta(T) = 0.4\beta_0 \times (1.5 + \frac{Tm - T}{Tm}).$$

Based on them, the temperature and pressure dependences of elasto-dynamic characteristics of the objects under study were determined. Some results of these calculations for six hydrides of group IV elements are listed in Table 1.

*Table 1.*Elasto-dynamic characteristics of Group 1V element hydrides

Hydride	Ti H	Zr H	Hf H
E_a, eV/at	3.8	4.7	5.0
β, 10^{11} Pa	10.2	12.6	13.4
T_m, K	1080	1330	1420
Θ_D, K	858	696	515
α_T, 10^{-6} K^{-1}	17	13.7	12.9
λ_f,J/cm.secK	0,52	0.643	0.685
C_P, J/g.K	1.61	3.13	3.57
ΔH, eV/at	- 3.79	-4.68	-4.98
ΔS, eV/(at.K)	$2.1.10^{-4}$	$2.9.10^{-4}$	$4.6.10^{-4}$
ΔΦ, eV/at	-3.73	-4.60	-4.84
Hydride	Ti H_2	Zr H_2	Hf H_2
E_a, eV/at	3.1	3.8	4.0
β, 10^{11} Pa	8.32	10.2	10.7
T_m, K	878	1080	1130
Θ_D, K	942	762	562
α_T, 10^{-6} K^{-1}	20.8	17	16.2
λ_f, J/cm.secK	0.424	0.520	0.548
C_P, J/g..K	1.37	1.96	3.15
ΔH, eV/at	-3.09	-3.79	-3.98
ΔS, eV/(at.K)	$1.8.10^{-4}$	$2.5.10^{-4}$	$4.1.10^{-4}$
ΔΦ, eV/at	-3.04	-3.71	-3.86

Table 2 contains the results of calculation of the same characteristics for hydrides of Group 1 *sp*-elements .

The data above make it possible to draw the following conclusions:

-the atom-atom interaction in Group 1V element hydrides becomes stronger with increasing the main quantum number of the Group 1V element.

-with increasing the ratio H/Me, the atom-atom interaction becomes weaker.

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Table 2. Elasto-dynamic characteristics of Group I element hydrides

Hydride	Na H	K H	Rb H
E_a, eV/at	1.93	1.79	1.73
β, 10^{11} Pa	6.08	1.85	1.56
T_m, K	546	507	490
Θ_D, K	922	473	303
α_T, 10^{-6} K^{-1}	33.5	36.1	37.3
λ_f, J/cm.secK	0.279	0.178	0.165
C_P, J/g.K	1.42	3.99	5.72
ΔH, eV/at	-1.92	-1.76	-1.69
ΔS, eV/(at.K)	$1.8.10^{-4}$	$5.1.10^{-4}$	$7.4.10^{-4}$
ΔΦ, eV/at	-1.87	-1.60	-1.47
Hydride	Na H_2	K H_2	Rb H_2
E_aeVэВ/at	2.00	1.90	1.85
β, 10^{11} Pa	5.04	1.96	1.67
T_m, K	566	538	524
Θ_D, K	1050	590	382
α_T, 10^{-6} K^{-1}	32.3	34	35
λ_f, J/cm.secK	0.268	0.189	0.176
C_P, J/g..K	1.14	2.94	5.07
ΔH, eV/at	-1.99	-1.88	-1.86
ΔS, eV/(at.K)	$1.5.10^{-4}$	$3.8/10^{-4}$	$6.5.10^{-4}$
ΔΦ, eV/at	-1.95	-1.77	-1.62

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- A comparative analysis of these data has established that with passage to Group 1 element hydrides the reguliarities become inverse.

The data calculated for pressure dependences of elasto- and thermo-dynamic characteristics are similar to the given in Table 3 for ZrH_2 .

Table 3. Pressure dependences of ZrH_2 properties

P,10^{11} Pa	0	0.1	1	3	5
β,10^{11}Pa	10	10	11	15	20
Eat,eV/at	4.7	4.7	5	5.5	7.2
-ΔH,eV/at	4.7	4.7	4.8	5	7.0
-ΔΦ,eV/at	4.6	4.6	4.7	4.9	6.8

As seen, with increasing pressure, the atom-atom interaction in these hydrides becomes stronger, which results in increasing the hydrogen saturation limit and may result in conservation of the metastable state of hydrogen after pressure relief.

To calculate the equilibrium hydrogen pressure over hydrides of any composition, a change in the free atomization energy ($\Delta\Phi_{пр}$) was analyzed for the following physicochemical transformation:

$$MeH_x=[Me]+x/2.H_2 \longrightarrow \Delta\Phi_{пр}(x).$$

Here $\Delta\Phi_{tr}(x)=\Delta\Phi(Me)+x/2.\Delta\Phi(H_2)-\Delta\Phi(MeH_x)$,

[Me] = 1/(1+x).

The thermo-dynamic equilibrium state was considered:

Ln K_P= $\Delta\Phi_{tr}(x)/(kT)$; $K_P=[Me].P^{X/2}_{H2}$.

From this we derived :

$P_{H2} = [(1+x).\exp(\Delta\Phi_{tr}(x)/(kT))]^{2/x}$.

With using the reference point adjustment to condensed hydrogen, the equilibrium hydrogen pressures and the corresponding "x" were calculated (Table 4).

Table 4. Hydride hydrogen saturation limits (values of x in MeH_X)

MeH_X	P,10^5Pa / T,°C	1	10	10^2	10^3
TiH_X	600	1.4	1.9	2.5	3.4
	700	1.0	1.4	1.9	2.7
	800	0.6	0.8	1.2	1.8
ZrH_X	600	2.4	3.1	3.9	5.3
	700	2.0	2.6	3.3	4.5
	800	1.6	2.0	2.7	3.7
HfH_X	600	3.0	3.8	4.9	6.5
	700	2.6	3.3	4.2	5.7
	800	2.2	2.8	3.6	5.0

As seen, under high hydrogen pressure hydrides with high degree of hydrogen absorption (up to MeH_7) can be produced. For this a special method for fixation of such states under normal conditions needs developing.

References

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