THERMODYNAMIC FUNCTIONS OF HIGH-PRESSURE ICES

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The modeling of Solar system giant planets satellites (Europa, Ganymede, Callisto, Titan, Triton) and other space objects containing water ices requires sufficient thermodynamic data on crystal H_2O phases stable at pressures inside considered bodies [1].

This study includes computations of basic thermodynamic potentials values for most of crystal forms of water ice – Ih, II, III, V, VI и VII, namely their Gibbs free energy, standard enthalpy and entropy.

Published experimental data on phase transitions in water-ice system, equations of state for water and ices, and reference data on water and simple substances O_2 and H_2 heat capacity were used as primary source data.

Computations were based on free energies of co-existing phases equality along phase transition curve condition:

$$\Delta G_1^0(T) + \int_1^P V_1 dP = \Delta G_2^0(T) + \int_1^P V_2 dP,$$

where ΔG_i^0 stands for i-th phase free energy variation at standard «zero» pressure (1 bar),

V_i is i-th phase molar volume, and i is 1 or 2.

Knowing ΔG^0 of one phase it is possible to compute ΔG^0 for an adjacent phase if equations of state for both phases are available and phase transition curve equation $T=T(P)$ is known.

Published equations of state for water and ices [4-8] and experimental data on phase transitions were used during computations. Experimental points were approximated with a $T(P) = a + b \cdot P + c \cdot P^{0.5} + d \cdot \ln(P) + e \cdot P^{-1}$ polynomial using coefficients from tab. 1 (T – K, P – bar). Resulting phase transition curves are presented in fig. 1.

Table 1

Phase transitions curves coefficients

|	a	b	c	d	e
L - Ih	273.0159	-0.0132	-0.1577	0.1516	0
L - III	10.277	0.0265	50.1624	0.5868	-4.3288
L - V	5.0321	-0.0004	30.9482	1.0018	0
L - VI	4.2804	-0.0013	21.8756	1.0018	1.0785
L - VII	-1355.42	0.0018	167.0609	-0.6633	0
L - X	0.2524	0.0019	0.2795	0.5	1.1675
Ih - II	0.2569	0.1026	0.2931	0.5	0.3789
Ih - III	18.9177	-0.3447	124.452	0.5709	0
II - III	1.2629	-0.0673	2.8096	1.0002	7.7816
II - V	6.6088	-0.028	36.2934	0.0086	0.7358
II - VI	1.0231	-0.3688	6.2306	0.501	30.7367
III - V	0.7846	0.1647	-0.5408	0.9999	-5.3526
V - VI	0.1181	0.4754	-5.8193	0.9997	-33.7273
VI - VII	-47.8507	0	-389.006	0.9932	28.8539
VI - VIII	-8.2483	0.0518	-81.5196	0.9991	0
VII - VIII	696.858	-0.0009	-52.7565	1.4191	0.8696
VII - X	28.3439	-0.007	331.927	1.0001	0
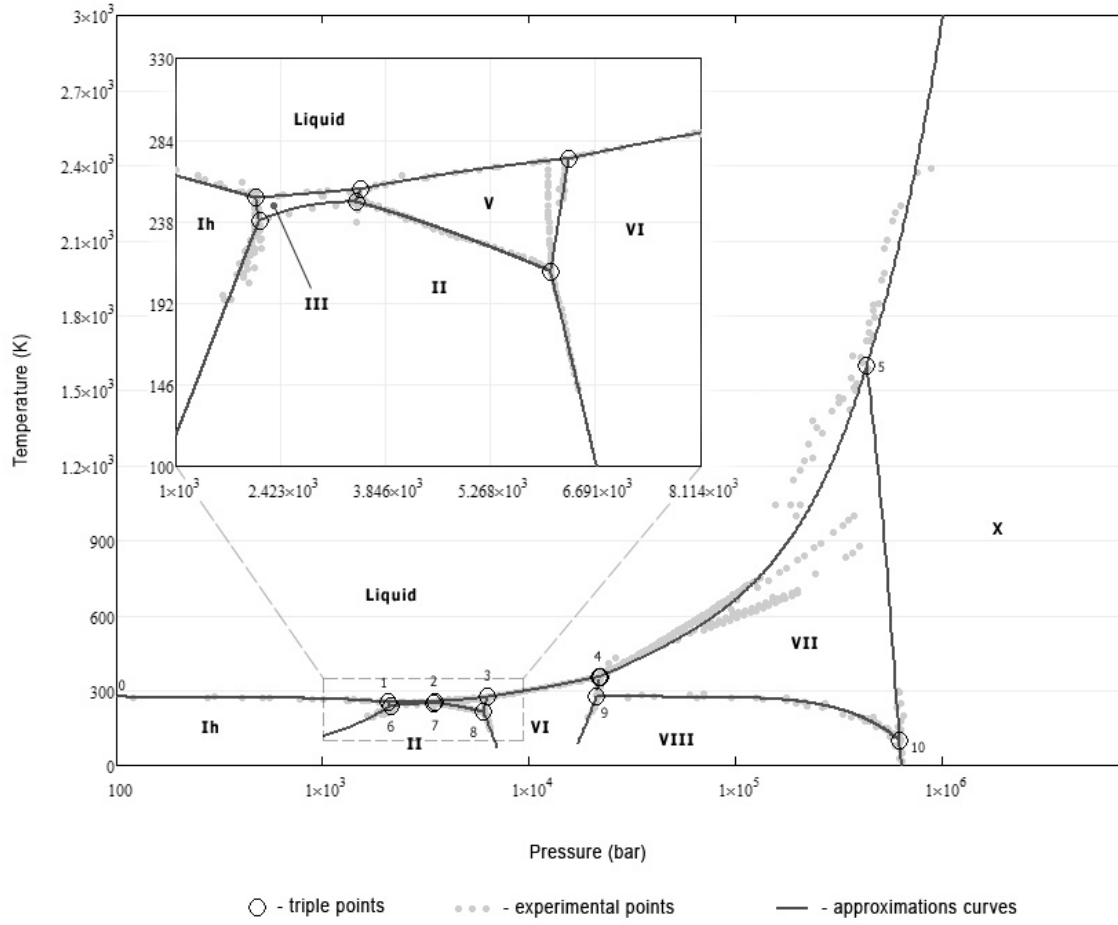
Fig.1. Experimental data on phase transitions and curves of approximations

ΔG^0 of ices VII, VI, V, II, III и Ih were consecutively calculated from water ΔG^0, which was derived from reference thermodynamic data on water, O₂, H₂ [2] according to method suggested in [3]:

$$\Delta G_L^0(T) = -288348.16 + 243.0913T - 10.6676T\ln(T) - 0.02113T^2 - 378756T^{-1}.$$

Knowing ΔG^0 of water it is possible to compute standard free energy variation functional dependence of temperature by computing ΔG_{VII}^0 values for a number of points on ice VII melting curve:

$$(\Delta G_{VII}^0)_i = \Delta G_L^0(T_i) + \int_1^{P_i} V_L(T_i, P)dP - \int_1^{P_i} V_{VII}(T_i, P)dP,$$

and making polynomial approximation for $\Delta G_{VII}^0(T)$. ΔG^0 of ices VI, V, II, III and Ih can be consecutively computed in the same way. Coefficients of resulting $\Delta G^0(T) = a + b{\cdot}T + c{\cdot}T^{0.5} + d{\cdot}\ln(T)$ polynomials are presented in Table 2.

Standard enthalpy ΔH^0 and entropy S^0 of ices can be derived from computed $\Delta G^0(T)$ according to:

$$\Delta S_i^0 = -\left(\frac{\partial G_i^0}{\partial T}\right)_P, \ \Delta H_i^0 = \Delta G_i^0 + T\Delta S_i^0, \ I = VII, VI, V, II, III, Ih$$

Resulting values are presented in tab. 2.

Thermodynamic functions values computed in this study can be used during phase equilibrium and phase composition computations in systems containing water and high pressure ices up to 25 kbar.

Table 2

Free energy, entropy and enthalpy computed values

Ice	$\Delta G°$ (J/moll)				$\Delta H°$ (kJ/moll)	$S°$ (J/moll·K)
	a	b	c	d		
Ih	-3.172×10^5	322.14	-6.512×10^3	1.704×10^4	-293.4	42.517
II	-2.865×10^5	237.946	-1.968×10^3	2.422×10^3	-292.1	44.163
III	-2.613×10^5	298.697	-3.68×10^3	0	-293.1	41.109
V	-2.833×10^5	213.276	-913.527	0	-291.2	46.432
VI	-2.829×10^5	213.88	-920.748	0	-290.9	46.037
VII	-1.825×10^5	45.8	9.811×10^3	-4.081×10^4	-289.5	40.25

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