

# ANALYTICAL EQUATIONS FOR P-V-T PROPERTIES OF HIGH-PRESSURE WATER ICES CALCULATIONS

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In outer regions of Solar system water and water ice become major components of internal structure of such planets as Uranium and Neptune, giant planets Jupiter and Saturn satellites (Europe, Ganimed, Kallisto, Titan, Entselad), small ice planets and asteroids located behind Neptune orbit, and also comets [1].

For the analysis of internal structure and composition of water containing space bodies the detailed thermodynamic information on phases formed in water-ice system is necessary.

In the present work various types of water high-pressure ices polymorphs equations of state available in literature are examined. Equations are tested to conform published experimental data best and to be convenient in their application to phase composition computations in water and high-pressure ices systems.

It seems that no uniform theoretical and thermodynamic base to define the universal form of high pressure ices equation of state (EOS) exists at the present time. Review of available experimental and theoretical works has shown that the following EOS types are often used for description of water ices P-V-T properties:

1. Third-order Birch-Murnaghan equation of state:

$$P = \frac{3}{2} K_{T^0} \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 - \frac{3}{4} (4 - K'_{T^0}) \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] \right\}, \text{ where}$$

$V_0$ ,  $T^0$  - molar volume at the standard pressure (1 bar) and standard temperature (usually 298 K);

$K_{T^0}$ ,  $K'_{T^0}$  - isothermal bulk modulus and its pressure derivative at standard temperature and pressure, respectively.

To use the Birch-Murnaghan EOS at non-standard temperatures it is necessary to define  $K_{T^0}(T)$  and  $V_0(T)$  dependences by the following formulas:

$$K_T(T) = K_{T^0}(T^0) + \left( \frac{\partial K_T}{\partial T} \right)_P (T - T^0),$$

$$V_0(T) = V_0(T^0) \exp \int_{T^0}^T \alpha(T) dT, \text{ where}$$

$\alpha(T)$  – pressure thermal expansion coefficient:  $\alpha(T) = 1/V_0 (\partial V_0 / \partial T)_P$ .

2. Vinet EOS, which has parameters similar to ones used in the previous equation:

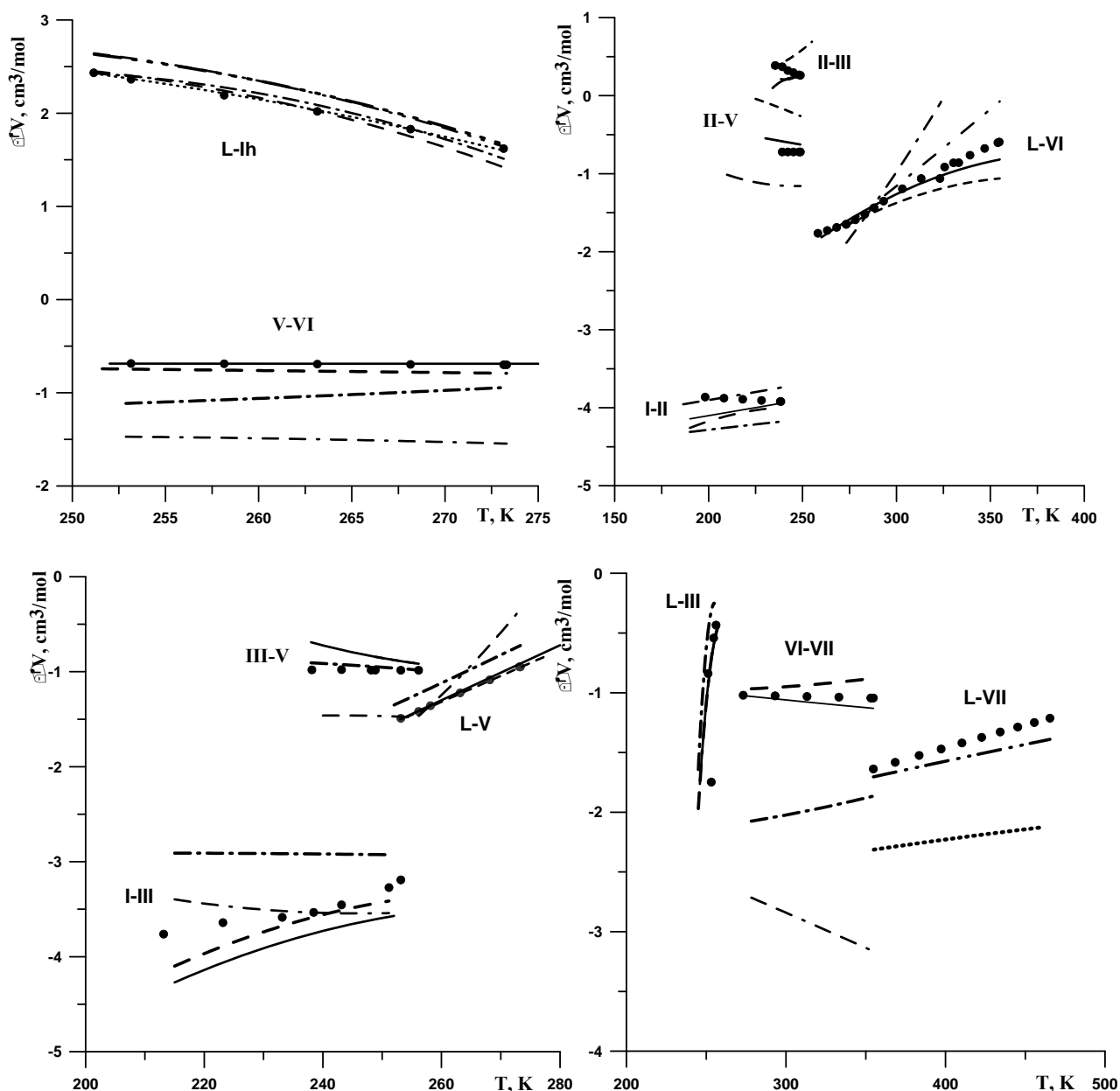
$$P = \frac{3K_{T^0}(1-x)}{x^2} \exp \left[ \frac{3}{2} (K_{T^0} - 1)(1-x) \right], \text{ где } x = \left( \frac{V}{V_0} \right)^{1/3}.$$

3. The fundamental equations of states on the basis of multiple parametric relations of Helmholtz  $F(\rho, T)$  and Gibbs  $G(P, T)$  free energies where independent variables are temperature T and respectively density  $\rho$  and pressure P.

4. The semiempirical equations of state in the form:  $V_i = V_i(T, P)$ .

The analysis of EOS types given above allows to notice that use of the Birch-Murnaghan and Vinet equations of state in changing T-P conditions assumes that compressibility and thermal expansion coefficients of water ices polymorphs are known. Such information can be obtained experimentally, however for the majority of H<sub>2</sub>O ices reliable experimental data is presently absent. This aspect essentially complicates these types EOS use at a wide range of temperatures and pressures.

At the same time the two last types of equations of state in most cases can be used in all range of thermodynamic stability of corresponding crystal phases when employed in explicit form. Thus these EOS are assumed to be the most convenient at thermodynamic calculations and are considered further in the present work.



**Fig.1.** Variation of water ices P-V-T properties on phase transitions lines.

Points – experimental data [2],

Lines – calculation from the EOS of ices I, II, III, V, VI, VII [3-10] and waters [11]:

Melting curves: —●●●— [3], —●●— [4], — — [5], — — [6], ●●●● [7],  
—●— [8], —●— [9].

Phase borders between ices polymorphs:

ices I-II: — — [3, 10], —●— [3, 5], — — [5], —●— [9];

ices I-III: — — [5], — — [3, 6], —●— [8], —●— [9];

ices II-III, II-V: — — [6, 10], — — [5], —●— [9];

ices III-V: — — [6], —●— [8], —●— [9];

ices V-VI: — — [5], — — [6], —●— [8], —●— [9];

ices VI-VII: — — [4, 5], — — [4, 6], —●— [4, 8], —●— [4, 9].

Fig. 1 shows how various types of equations of state describe variation of P-V-T properties of crystal ices and liquid water along the phase transitions lines in the water-ice system. The following equations of state published in experimental and theoretical works were used during calculations: [11, 3, 4, 10] – EOS of water and ices Ih, II, VII, respectively, [5, 9] – EOS of ices Ih, II, III, V, VI, [6] – EOS of ices III, V, VI, [7] – EOS of ices Ih, II, III, V-VII, [8] – EOS of ices I, III, V, VI. Experimental data on molar volumes variation at phase transitions was obtained from [2].

Performed calculations show that the equations of state offered in [7], adequately describe P-V-T properties of ice Ih only, leading to very significant error in case of other ices (ices II, III, V, VI, calculated from these EOS are not shown on fig. 1 because of that).

The ices I, II, III, V, VI equations of state from [8] reproduce ices experimental melting curves well within the H<sub>2</sub>O developed model. However their use together with other EOS and their application for the solid phase transitions between various forms of water ices description do not always give satisfactory results.

I, II, III, V, VI ices equations of states, deduced on the basis of known models of water TIP4P/2005 and TIP4P/Ice in [9], are in the good consent with experiment along separate isotherms within the field of stability of corresponding ice phase. However the ices and water P-V-T properties variation along the phase transitions curves are described by these EOS with a considerable error.

The best agreement with experiments is given by the following EOS: for ices Ih, II and VII – works [3, 10, 4] accordingly, for ices III, V, VI – work [6]. Thus, it is possible to conclude, that these equations of state that are most suitable for description of H<sub>2</sub>O crystal ices P-V-T properties.

The listed EOS have been further used for the calculation of major thermodynamic characteristics (standard free energy of formation, entropy, and enthalpy) of H<sub>2</sub>O high pressure ices.

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