

Equations of temperature dependence of ice capacity and some clathrate hydrates formed in H–O–C–N–Ar–Kr–Xe system at low temperatures and pressure

V. A. Dorofeeva^{1,2}, O. V. Vagina²

¹ V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Moscow

² Dubna International University of Nature, Society, and Man, Dubna

dorofeeva@geokhi.ru

For the study of phase equilibrium in H–O–C–N–Ar–Kr–Xe system at low temperatures ($T < 100\text{K}$) and pressure ($P < 10^{-6}$ bar) we were obtained coefficients of semi-empirical equation of the temperature dependence of heat capacity for ice, $\text{CO}_2(\text{cr})$ и $\text{NH}_4\text{OH}(\text{cr})$ proposed by I.L. Khodakovsky

Key words: cosmochemistry, modeling, thermodynamics, heat capacity, ice, clathrate hydrates

Citation: Dorofeeva, V. A., O. V. Vagina (2012), Equation of temperature dependence of ice capacity and some clathrate hydrates formed in H–O–C–N–Ar–Kr–Xe system at low temperatures and pressure, *Vestn. Otd. nauk Zemle, 4, NZ9001*, doi:10.2205/2012NZ_ASEMPG

One of the most important problems of modern cosmochemistry is genesis of volatiles in Titan and Enceladus which are regular satellites of Saturn. During the space mission «Cassini» it was found that the main components of the atmosphere Titan are nitrogen and methane and there are in significant quantities NH_3 , N_2 , CH_4 , CO и CO_2 in the plume of Enceladus. Heretofore, their origin isn't known – whether it was the primary gases of the solar protoplanetary disk (nebula), accumulated by ice planetesimals, which were formed in the area of Saturn, some of them have already been formed in the bowels of the satellites in the action of their evolution. Model reconstruction of the accumulation of volatiles from the nebula gas phase requires thermodynamic information for all components potentially possible in H–O–C–N–Ar–Kr–Xe system, including condensed phases, crystalline and clathrate hydrates formed in the solar system composition at low temperatures ($T < 100\text{K}$) and pressures ($P < 10^{-6}$ bar).

However thermodynamic information for a number of condensed and solid phases as well as clathrate hydrates in these PT conditions is not full enough. This is due to the fact that in the Earth's formation of such phases is associated with much higher pressures and temperatures than in a nebula, for example, the formation of methane clathrate hydrate methane in the deep sea.

Moreover all the necessary experimental information is fragmentary and often not easily accessible. Unfortunately nowadays there are not reference books providing us with the results of experimental measurements and recommended values of thermodynamic and thermoelastic properties of substances for the temperature range from 0 to 273 K.

It is necessary to have the equation of heat to get functional dependencies of the thermodynamic properties of these components on temperature: $C_p = C_p(T)$.

Table 1 presents the results of experimental data search based on heat capacity measurements for some substances as well as the temperatures in which the measure passed.

The semi-empirical equation of the temperature dependence of heat capacity $C_p(T)$ proposed by I.L. Khodakovsky was used as an analytical function.

$$C_p = Rn[kL_D + (3 - k)L_E] + \alpha_T^2 V_T K_T T \quad (1),$$

where $L_D = [1 - 1/(1 + bT^3)]$, $L_E = [1 - 1/(1 + cT^2)]$,

R – gas constant, n – the number of atoms in a molecule,

α_T – volume coefficient of thermal expansion,

K_T – isothermal bulk modulus,

V_T – volume of one gram mole of a substance,

DOROFEEVA ET AL: EQUATIONS OF TEMPERATURE DEPENDENCE

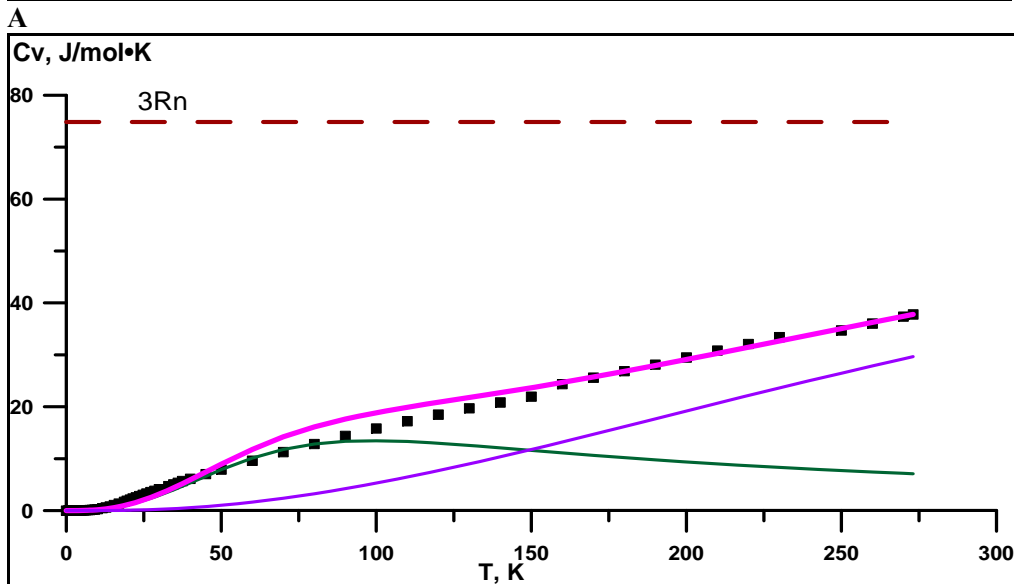
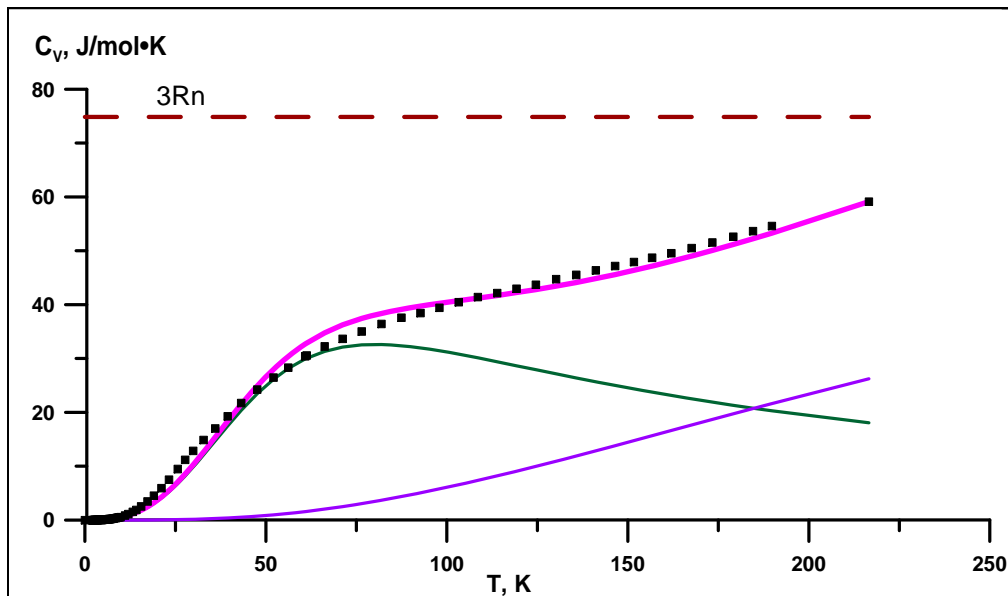
T – temperature,
B, c and *k*, – empirical coefficients.

Table 1. Experimental data of measurements of a thermal capacity for substances under consideration

System	T (K) for C_p	Reference
Kr	0.4–12	[Finegold et al, u òp, 1969]
Xe		
H ₂ O(cr)	0.5–38 40–273.15	[Smith et al, 2007] [Giauque et al, 1936] [Glushko et al, 1978]
CO(cr)	0.8–4.2	[Burford et al, 1969]
CO ₂ (cr)	2–20 15–195	[Manzhelii et al, 1971] [Giauque et al, 1937]
CH ₄ (cr)	0.4–28	[Vogt et al, 1976]
Kr·5.66H ₂ O(cr)	7–115 85–270	[Handa et al, 1989] [Handa et al, 1986]
Xe·6.176H ₂ O(cr)	7–160 85–270	
CH ₄ ·5.75H ₂ O(cr)	85–270	[Handa et al, 1986]
NH ₄ OH(cr)	15–300	[Chan et al, 1964]
NH ₃ ·2H ₂ O(cr)	15–300	[Chan et al, 1964]

Temperature dependence of the empirical parameter *k* which changes within the range from 3 to 0, can be presented by the following equation: $k = 9/(9 + xT^2)^{1/2}$. If $T \rightarrow 0$ and $k = 3$, the first term in square brackets of equation (1) gives the contribution to the heat capacity is described by Debye's theory ($C_v = AT^3$). If $T > 10-40$ K will become a significant contribution to the heat capacity is described by Einstein's theory [Khodakovsky, 2012]. A relative value of both contributions to the value of specific heat, varying with temperature is regulated with the help of *k* (*T*).

Today, as a first approximation, to calculate the difference between $C_p - \alpha^2 VTK_T = C_v$ values of α_T , V_T and K_T used at standard temperature, which in the case of crystalline compounds is the melting point of ice. Using equation (1) we carried out calculations for ice, CO₂(cr) and NH₄OH(cr), which are presented in table 2. Unfortunately, we were not able at this stage to find in the literature the data of α_T , V_T and K_T at the standard temperature for the NH₄OH(cr) allow a difference therefore the first phase of work we have taken condition they are equal to zero and put $C_p \approx C_v$. The results of fitting the experimental data for CO₂(cr) and H₂O(cr) are shown in Fig. 1 and 2, as well as the contributions that vary with temperature.



A
B
Fig. 1. **A** – Temperature dependence of heat capacity for $\text{CO}_2(\text{cr})$, ■ experiment, Azer-Ainou 2005, ● experiment, [Manzeli 1971]. **B** – Temperature dependence of heat capacity for $\text{H}_2\text{O}(\text{cr})$. ■ experiment, Smith и др 2007, recommended [Glushko et al, 1978], — calculation by equation (1), — the contribution to the heat capacity, described the first term of equation (1), conventionally designated as L_D , — the contribution to the heat capacity, as described by the second term of equation (1), conventionally designated as L_E , — upper limit of the temperature dependence of heat capacity

Table 2. Result of calculation of the equation's (1) coefficients

System	b	c	x	$\alpha_T^2 V_T K_T T$ (Дж/МОЛЬ·К)	$\Delta \text{otn}\%$
$\text{H}_2\text{O}(\text{cr})$	$2.31 \cdot 10^{-5}$	$0.10 \cdot 10^{-4}$	0.0127	1.038	14.6
$\text{CO}_2(\text{cr})$	$0.66 \cdot 10^{-6}$	$0.18 \cdot 10^{-4}$	0.003	$1.48 \cdot 10^{-3}$	4.3
$\text{NH}_4\text{OH}(\text{cr})$	$0.29 \cdot 10^{-5}$	$0.19 \cdot 10^{-4}$	0.0262	0	8.0

DOROFEEVA ET AL: EQUATIONS OF TEMPERATURE DEPENDENCE

From the data of Tab. 2 the values of relative errors, we see that equation (1) adequately describes the temperature dependence of specific heat $\text{CO}_2(\text{cr})$ and $\text{NH}_4\text{OH}(\text{cr})$, and the calculated values accord with the experimental data. At the same time, for the $\text{H}_2\text{O}(\text{cr})$ the value of the relative error was very high. However, as can be seen from Fig. 2, the largest deviation values calculated by equation (1), from the experimental data is observed in the range $T = 80\text{--}150\text{K}$. Perhaps this is due to the transition of ice in the glassy state in this temperature range, and therefore the complexity of the experiment, as noted by the authors [Giauque, 1936; Smith, 2007]. In consequence of this there is doubt that in the interval $T = 80\text{--}150\text{K}$ the measured values of heat capacity are in equilibrium.

In conclusion, it should be noted that probability of error will be lower if we use the resulting values for solving the problem of obtaining the enthalpy and entropy which are integral functions in the given range of temperatures.

The work was performed under RAS Presidium Program №22.

Reference

- Glushko, V. P., L. Gurevich, G. Bergman. (1978). *Thermodynamic properties of individual substances*, v. 1, Moscow.
- Khodakovskiy, I. L. (2012). A New Semi-empirical Equations of Temperature Dependences of Heat Capacity and Thermal Expansion Coefficient for inorganic substances, *Vestnik ONZ RAN*, 4, (doi:).
- Azger-Ainou, M. (2005). Low-temperature data for Carbon Dioxide, *Monatshefte fur Chemie Chemical Monthly*, 136, 2017–2027.
- Chan, J. P., W. F. Giauque (1964). The Entropy of $\text{NH}_3 \cdot 2\text{H}_2\text{O}$. Heat Capacity from 15 to 300°K , *J. Phys. Chem.*, Vol. 68, N 10, 3053–3057.
- Chan, J., W. Giauque (1964). Additions and Corrections-The Entropy of $\text{NH}_3 \cdot 2\text{H}_2\text{O}$. Heat Capacity from 15 to 300K , *J. Phys. Chem.*, Vol. 68, N 12, 3912/
- Graham, B. (1969). Heat capacities of O_2 , N_2 , CO , and NO at low temperatures, *Canadian Journal of Physics*, 47(1): 23-29, 10.1139/p69-004.
- Finegold, L. (1969). Low-Temperature Heat Capacities of Solid Argon and Krypton, *Phys. Rev.*, 177, 1383–1391.
- Jager A., Span R. (2012). Equation of State for Solid Carbon Dioxide Based on the Gibbs Free Energy, *J. Chem. Eng. Data*, 57, 590–597.
- Handa, Y. P. (1986). Calorimetric determinations of the compositions, enthalpies of dissociation, and heat capacities in the range 85 to 270K for clathrate hydrates of xenon and krypton, *J. Chem. Thermodyn.*, vol. 18, N 10, 891–902.
- Handa, Y. P., O. Yamamuro, M. Oguni and H. Suga (1989). Low-temperature heat capacities of xenon and krypton clathrate hydrates, *J. Chem. Thermodyn.*, 21, 1249.
- Handa, Y. P. (1986). Compositions, enthalpies of dissociation, and heat capacities in the range 85 to 270K for clathrate hydrates of methane, ethane, and propane, and enthalpy of dissociation of isobutane hydrate, as determined by a heat-flow calorimeter, *J. Chem. Thermodyn.*, vol. 18, N 10, 915–921.
- Giauque, W. F., J. W. Stout (1936). The Entropy of Water and the Third Law of Thermodynamics. The Heat Capacity of Ice from 15 to 273°K , *J. Amer. Chem. Soc.*, vol 58, N 7, 1144–1150
- Manzhelii, V. G., A. M. Tolkachev (1971). Thermal Expansion, Heat Capacity, and Compressibility of Solid CO_2 , *Phys. stat. sol. (b)* 44, 39.
- Smith, S. J, B. E. Lang, S. Liu, J. Boero-Goates, B. F. Woodfield (2007). Heat capacities and thermodynamic function of hexagonal ice from $T=0.5\text{K}$ to $T=38\text{K}$, *J. Chem. Thermodynamics*, 39, 712–716.
- Vogt, G. J., K. S. Pitzer (1976). Entropy and heat capacity of methane, spin species conversion, *J. Chem. Thermodyn.*, v. 8, is. 11, p. 1011–1031.