

The heat capacity of water ice in interstellar or interplanetary conditions

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Abstract. Three empirical equations are proposed to describe the existing experimental data on the heat capacity of water ice for $0\text{ K} \leq T \leq 273\text{ K}$. This may be important for the rate of non-stationary thermal processes at very low temperatures in cometary nuclei or cosmogonical scenarios.

Key words. ISM: molecules – comets: general – stars: formation

The heat capacity of water ice is often used in cometary physics and in cosmogonical calculations. Water vapour is an important component of protostellar clouds. Its condensation into icy grains is a common feature of any cosmogonical scenario. Theoreticians usually take the heat capacity from glaciology. I used in my calculations (Shulman 1987) the relationship

$$C_p = 7.8 \times 10^{-3} T \text{ J g}^{-1} \text{ K}^{-1} \quad (1)$$

which is given in the handbook by Bogorodsky & Gavrilov (1980), while other authors, e.g. Klinger (1981) and Prialnik (1992) used Klinger's formula

$$C_p = 7.49 \times 10^{-3} T + 0.09 \text{ J g}^{-1} \text{ K}^{-1} \quad (2)$$

which is based on the experimental data of Giauque & Stout (1936).

Equation (2) is in obvious contradiction with the Nernst heat theorem, but both (1) and (2) are wrong at low temperatures. Really, no one of them gives the low temperature heat capacity of ice which is described by the Debye-Sommerfeld equation

$$C_p = \frac{12\pi^4 k}{5m\theta_D^3} \cdot T^3 \quad (3)$$

where k is Boltzmann's constant and m is the mass of a water molecule.

Giauque & Stout (1936) measured the heat capacity in the interval $16.43\text{ K} \leq T \leq 267.77\text{ K}$. Measurements in the interval $2.144\text{ K} \leq T \leq 27.034\text{ K}$ were carried out by Flubacher et al. (1960). However both (1) and (2) are valid only for $T > 100\text{ K}$ as shown by Fig. 1. So we need a better approximation for the heat capacity of ice at low temperatures.

To get such an approximation, the original data measured by Giauque & Stout (1936) was combined with those of

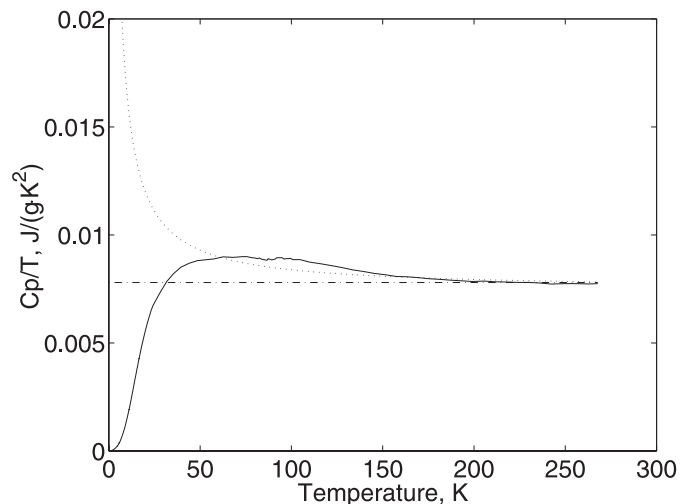


Fig. 1. The discrepancy between the experimental data (solid curve) and the empirical Eq. (1) – dash dotted curve and Eq. (2) – dotted curve.

Flubacher et al. (1960) and with the theoretical values calculated for $T \leq 2.5\text{ K}$ by Eq. (3). The Debye temperature $\theta_D = 152\text{ K}$ given by Weast (1975) is not compatible with the Flubacher et al. data. The value $\theta_D = 222.2\text{ K}$ was taken for the vicinity of absolute zero. Then the whole set was processed to obtain the best accuracy with the minimal number of parameters.

A simple polynomial approximation is not applicable. A very good approximation is given by the formula

$$C_p = 7.73 \times 10^{-3} T \left(1 - e^{-1.263 \times 10^{-3} T^2}\right) \times \left(1 + e^{-3\sqrt{T}} \times 8.47 \times 10^{-3} T^6 + 2.0825 \times 10^{-7} T^4 e^{-4.97 \times 10^{-2} T}\right). \quad (4)$$

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Table 1. The experimental data by Flubacher et al. versus Eqs. (4), (5).

T	Experiment	Empirical formulae			T	Experiment	Empirical formulae		
		(4)	(5)	(6)			(4)	(5)	(6)
2.14	0.0001	0.0001	-0.0022	-0.0015	7.91	0.0067	0.0067	0.016	0.015
2.55	0.00015	0.00016	-0.0011	-0.0005	8.79	0.0096	0.0096	0.0196	0.0189
2.59	0.00017	0.00017	-0.001	-0.0004	8.90	0.0100	0.0101	0.0201	0.0194
2.69	0.00018	0.00019	-0.00077	-0.0002	9.87	0.0145	0.0144	0.0246	0.0237
2.80	0.00021	0.00022	-0.0005	0.0001	9.96	0.0149	0.0148	0.025	0.0241
3.09	0.00030	0.00030	0.0003	0.0008	11.10	0.0213	0.0213	0.0308	0.0297
3.11	0.00030	0.00030	0.0004	0.0008	11.11	0.0213	0.0214	0.0309	0.0298
3.18	0.00033	0.00033	0.0006	0.001	11.46	0.0237	0.0237	0.0328	0.0317
3.58	0.00046	0.00047	0.0016	0.002	12.23	0.0290	0.0291	0.0372	0.0359
3.65	0.00048	0.00050	0.0018	0.0022	12.43	0.0308	0.0307	0.0384	0.0371
3.67	0.00051	0.00051	0.0019	0.0022	12.55	0.0317	0.0316	0.0391	0.0378
3.73	0.00054	0.00053	0.0020	0.0023	13.53	0.0398	0.0397	0.0452	0.0439
4.04	0.00070	0.00070	0.0030	0.0032	13.54	0.0402	0.0398	0.0453	0.044
4.14	0.00072	0.00075	0.0032	0.0034	14.51	0.0493	0.0488	0.0519	0.0505
4.15	0.00074	0.00076	0.0033	0.0034	14.62	0.0502	0.0500	0.0527	0.0513
4.65	0.0011	0.0011	0.0047	0.0048	15.52	0.0596	0.0591	0.0593	0.0578
4.74	0.0011	0.0012	0.0050	0.0050	15.61	0.0602	0.0600	0.0599	0.0584
4.76	0.0011	0.0012	0.0050	0.0051	16.50	0.0706	0.0697	0.0669	0.0654
5.18	0.0015	0.0016	0.0063	0.0063	16.57	0.0708	0.0705	0.0674	0.0659
5.27	0.0016	0.0017	0.0066	0.0066	17.44	0.0805	0.0804	0.0747	0.0731
5.74	0.0022	0.0022	0.0081	0.0078	17.83	0.0853	0.0850	0.078	0.0764
5.74	0.0021	0.0022	0.0081	0.0080	18.96	0.0984	0.0987	0.0881	0.0865
5.80	0.0022	0.0023	0.0083	0.0081	19.74	0.1079	0.1084	0.0955	0.0938
6.26	0.0030	0.0030	0.0099	0.0096	21.06	0.1245	0.125	0.1085	0.1068
6.72	0.0038	0.0038	0.0115	0.0111	23.11	0.1501	0.1509	0.1301	0.1284
6.74	0.0038	0.0038	0.0115	0.0111	25.09	0.1747	0.1758	0.1524	0.1508
7.25	0.0049	0.0050	0.0134	0.0129	27.03	0.1981	0.1996	0.1754	0.1738
7.80	0.0064	0.0064	0.015	0.015					

The following expression with the same number of constants is simpler but gives worse accuracy:

$$C_p = 7.73 \times 10^{-3} T \left(1 - e^{-1.263 \times 10^{-3} T^2} \right) - 7.59 \times 10^{-3} + 2.509 \times 10^{-3} T - 1.472 \times 10^{-5} T^2 - 1.617 \times 10^{-9} T^3 + 8.406 \times 10^{-11} T^4. \quad (5)$$

The polynomial approximation could be improved by increasing the number of constants, e.g.:

$$C_p = 7.73 \times 10^{-3} \left(1 - e^{-1.263 \times 10^{-3} T^2} \right) - 6.22 \times 10^{-3} + 2.181 \times 10^{-3} T - 3.73 \times 10^{-6} T^2 - 1.286 \times 10^{-7} T^3 + 6.7 \times 10^{-10} T^4 - 9.34 \times 10^{-13} T^5. \quad (6)$$

The first term, which ensures the asymptotic behaviour of the heat capacity, should not be omitted. The expressions give the heat capacity in the same units as Eq. (1). Tables 1 and 2 demonstrate the quality of the approximation.

The difference experiment–approximation is shown in the Fig. 2. These deviations are very small (Fig. 3).

To calculate the enthalpy of ice

$$H = \int_0^T C_p(T) dT \quad (7)$$

with 30%-accuracy in the low temperature region the simple relationships (1) and (2) may be applied as shown by Fig. 4.

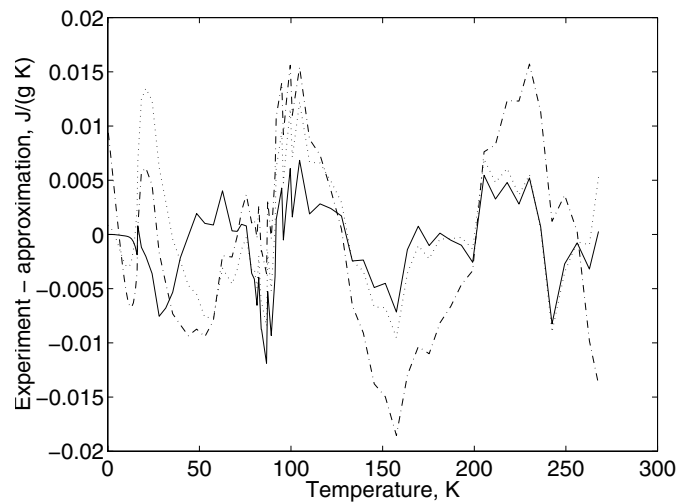
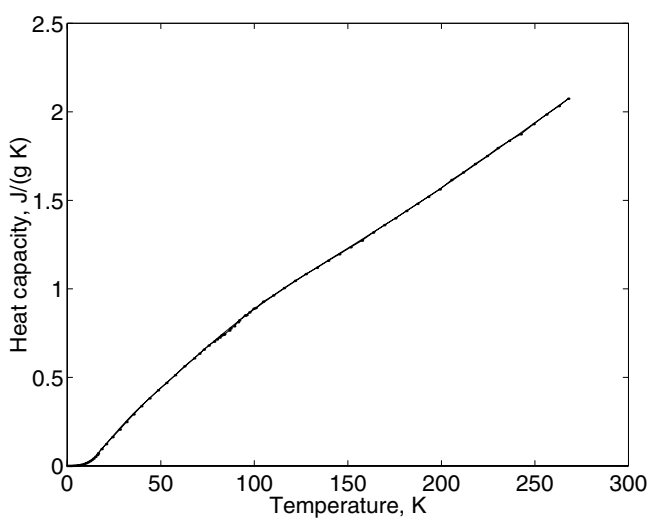
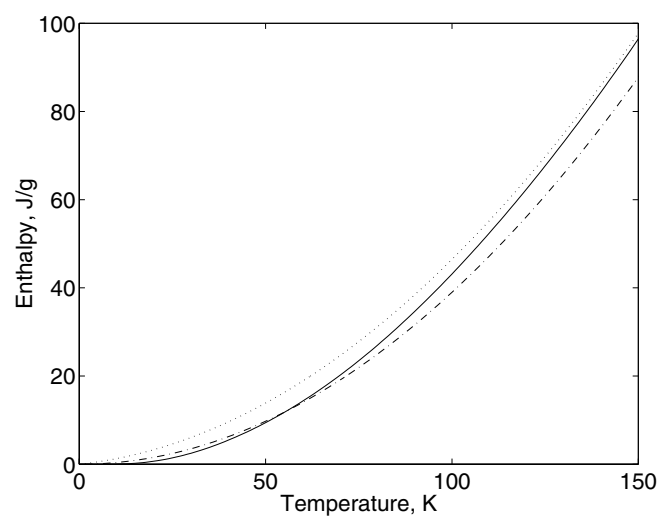


Fig. 2. The difference experiment–approximation for the relationships (4) – solid line, (5) – dash dotted, and (6) – dotted line.

Taking into consideration this correction to the low temperature heat capacity of water ice one can see that the same energy heats ice to a higher temperature. So any process whose rate is described by an activation law $\tau \propto \exp(E_a/kT)$ proceeds in shorter time. The crystallization of amorphous ice is an example of such a process.

Table 2. The experimental data by Giauque and Stout versus Eqs. (4)–(6).

T	Experiment	Empirical formulae			T	Experiment	Empirical formulae		
		(4)	(5)	(6)			(4)	(5)	(6)
16.43	0.07053	0.06894	0.06634	0.06479	99.57	0.8878	0.8821	0.8726	0.8736
18.37	0.09544	0.09153	0.0828	0.08115	100.69	0.892	0.8907	0.881	0.882
20.78	0.1229	0.1214	0.1057	0.104	104.69	0.9276	0.921	0.9112	0.9119
24.20	0.1629	0.1647	0.1423	0.1406	110.13	0.9628	0.961	0.9516	0.9519
28.05	0.2055	0.2118	0.1878	0.1862	115.84	1.004	1.002	0.9935	0.9934
31.64	0.2479	0.2531	0.2326	0.2312	121.74	1.045	1.043	1.036	1.036
35.46	0.2912	0.2945	0.281	0.2798	127.54	1.084	1.082	1.078	1.076
39.62	0.3373	0.3375	0.3329	0.332	133.50	1.119	1.122	1.12	1.118
43.96	0.382	0.381	0.3846	0.3841	139.48	1.159	1.161	1.161	1.159
48.52	0.4276	0.4258	0.4356	0.4355	145.43	1.195	1.2	1.203	1.2
52.98	0.4688	0.4691	0.4821	0.4824	151.43	1.235	1.24	1.244	1.241
57.66	0.5128	0.514	0.5277	0.5284	157.48	1.272	1.28	1.285	1.282
62.63	0.5629	0.5612	0.5734	0.5743	163.52	1.318	1.32	1.326	1.323
67.83	0.608	0.6099	0.6189	0.6201	169.42	1.36	1.359	1.366	1.363
70.61	0.6339	0.6356	0.6425	0.6438	175.36	1.398	1.399	1.406	1.403
73.01	0.6567	0.6576	0.6625	0.664	181.25	1.44	1.44	1.446	1.443
75.60	0.6802	0.681	0.6839	0.6854	187.20	1.48	1.481	1.486	1.484
78.51	0.7021	0.707	0.7076	0.7092	192.96	1.52	1.521	1.525	1.524
79.98	0.7146	0.72	0.7195	0.7211	199.11	1.562	1.565	1.567	1.566
81.44	0.7251	0.7328	0.7313	0.7328	205.32	1.614	1.609	1.609	1.61
82.42	0.7363	0.7413	0.7391	0.7407	211.56	1.657	1.654	1.653	1.654
83.72	0.7428	0.7526	0.7495	0.751	217.97	1.705	1.701	1.698	1.7
83.94	0.7447	0.7544	0.7512	0.7528	224.36	1.75	1.747	1.743	1.746
86.66	0.7649	0.7776	0.7728	0.7743	230.08	1.795	1.79	1.785	1.788
87.25	0.7765	0.7826	0.7774	0.7789	236.19	1.836	1.835	1.83	1.833
89.20	0.7889	0.7989	0.7927	0.7942	242.40	1.873	1.882	1.876	1.88
91.32	0.8119	0.8164	0.8092	0.8106	249.31	1.931	1.934	1.929	1.932
91.93	0.8222	0.8214	0.8139	0.8153	256.17	1.985	1.985	1.984	1.984
94.93	0.8494	0.8456	0.8371	0.8384	262.81	2.033	2.036	2.038	2.035
95.85	0.852	0.8529	0.8442	0.8454	267.77	2.074	2.074	2.079	2.074
97.37	0.8669	0.8649	0.8558	0.857					

**Fig. 3.** The experimental data (circles) versus the approximation (4) – solid line.**Fig. 4.** The same as in Fig. 1 for enthalpy. The solid line shows the enthalpy calculated from experimental data (the approximation (4) gives the same curve) while the dash dotted and dotted lines are obtained using (1) and (2).

Equations (4)–(6) describe the heat capacity of crystalline ice but there is no reason for a big difference between these quantities for amorphous and crystalline ice. The heat capacity is formed by energy distribution on the degrees of freedom. Since water ice is a molecular crystal where molecules retain their individuality, the difference between the heat capacities should be of the same order as the difference between their heats of sublimation. The same assumption for the transfer properties of both states of ice would be wrong because the transfer properties are defined by the free path of the corresponding carrier: phonons for the heat transfer, H_3O^+ and OH^- ions for electric conductivity, etc. Any free path is much shorter in amorphous ice which can be considered as having an extremely high concentration of dislocations.

Some authors mistakenly write that there are species for which the Nernst theorem is not fulfilled. The heat capacity of some species (for example, lanthanides and their compounds) has one or more sharp peaks at the extremely low temperature where the contribution of the inner degrees of freedom (the energy of inner electron envelopes, nuclear spins etc) becomes essential. Nevertheless the heat capacity should go to zero at $T \rightarrow 0$. In the vicinity of these peaks the Debye-Sommerfeld formula (3) is incorrect but it does not disprove the third principle of thermodynamics.

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