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ISOBARIC HEAT CAPACITY OF SEAWATER

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The values of isobaric heat capacity of seawater over the interval of temperature $0 \leq t \leq 40$ °C, salinity $0 \leq S \leq 40$ and pressures $0 \leq p \leq 130$ MPa have been calculated and derived the approximating equation. The relative uncertainty of the heat capacity data depending on parameters of states lies within 0.05-0.08 %. The obtained results are compared to literature data. The behavior of the heat capacity of water under influence S, t, p -factors is discussed briefly.

Introduction. The rational use of the power, mineral and biological resources of World Ocean demands the comprehensive investigation of physicochemical properties of seawater (SW). For solving of some problems in oceanology, climatology and ecology it is necessary to have the precise calorific data for seawater. The heat capacity data represent also certain interest for designing and operation of the desalination installations.

It is known that the seawater is the low concentration multicomponent electrolyte solution. From this point of view the heat capacity data can be used as for construction of theoretical models of multicomponent electrolyte solutions, and in various thermodynamic calculations.

The purpose of the present work – calculation of C_p of seawater in the above-mentioned region of parameters of state by using the equation of state (EOS), developed before [1].

The experimental researches of the isobaric heat capacity of SW are not numerous. They are carried out at atmospheric pressure or in the saturation condition. The first measurements of heat capacity of SW were carried out by Thoulet and Chevallier 120 years ago [2]. The data was derived at isotherm 17.5 °C and in the salinity interval 0-40 ‰. In spite of the fact that results of this work the long time were unique and were applied by oceanologists of the all world, now they have become outdated, and because of low accuracy can have only historical interest.

The measurements of Cox and Smith [3] cover the interval of temperature 2-31 °C and salinity 0-40 ‰. The uncertainty of experimental data, according to authors, does not exceed ± 0.05 %. Bromley et al. [4] have carried out measurements of C_p in the interval of salinity 10-120 ‰ and temperatures 2-80 °C, and later [5] have expanded the range of temperatures up to 200 °C.

Millero et al. [6] have carried out the measurements of C_p using flow calorimeter in the interval chlorinity 0.5-22 ‰ (1-40 ‰ salinity) and temperature 5-35 °C, with step 10 °C. As an experimental sample the standard seawater was used. The seawater solutions various salinity were prepared by its evaporation or dilution. The good agreement was found with results of the previous measurements [3,4] (the deviations basically are within ± 0.05 %). However at low temperatures the deviations from measurements of Cox and Smith [3] are reaching 0.15 %. On the basis of results of own measurements Millero et al. [7] have derived the equation for heat capacity of SW, applicable in the interval of temperature 0-35 °C and salinity 0-40, according to PSS-78 salinity scale.

The measurements of heat capacity of seawater under high pressures till now were not carried out. It may be explained, on the one hand, complexity and difficulty of experimental investigations at high pressures, and on the other hand that pressure dependence of heat capacity can be easily derived using PVTs-measurements or EOS.

The UNESCO tables [8] for heat capacity of SW, covering the interval of pressure 0-100 MPa, are calculated using the International equation of state of seawater EOS-80 [7]. Reliability of these tables is low, as it was shown by us earlier [1], that the equation EOS-80 poorly transfers the derivative properties of the thermodynamic PVTs-surface. This circumstance is the basic argument for performing of new calculations of isobaric heat capacity of SW by use of more precise thermal data.

Computation procedure and the initial data. The pressure change of isobaric heat capacity was computed with help of the known differential relation of thermodynamics, binding thermal and calorific properties of substance

$$\left(\frac{\partial C_p}{\partial p} \right)_{T,S} = -T \left(\frac{\partial^2 v}{\partial T^2} \right)_{p,S} . \quad (1)$$

After its integration we receive

$$Cp(S,t,p) = Cp(S,t,0) - T \int_0^p \frac{\partial^2 v}{\partial T^2} dp, \quad (2)$$

where T – is the absolute temperature; $t = T - 273.15$; v – is the specific volume; $Cp(S,t,p)$ and $Cp(S,t,0)$ are respectively the isobaric heat capacity of SW at pressure p and at atmospheric pressure.

For computation of the heat capacity of SW at atmospheric pressure $Cp(S,t,0)$ the formula of Millero et al. [7] can be used. However, this formula contains the uncertainty, depending on temperature. In this connection, from the formula, given in [7] was borrowed only the salinity decrement of heat capacity [$Cp(S,t,0) - Cp(0,t,0)$], and the equation for temperature dependence of heat capacity of pure water $Cp(0,t,0)$ is derived by us anew

$$Cp(0,t,0) = 4218.752 - 3.663389t + 0.1292775t^2 - 2.205117 \cdot 10^{-3}t^3 + 1.562835 \cdot 10^{-5}t^4, \quad (3)$$

Equation (3) is valid over the temperature range 0-40 °C, according to IPTS-68 temperature scale.

The second term in right part of the equation (2) was computed by double differentiation the EOS [1] with respect to temperature and the subsequent integration with respect to pressure. We shall remind that the EOS [1] was derived on the basis of the sound speed data, therefore provides higher accuracy of calculation of the derivative $\partial^2 v / \partial T^2$. All mathematical operations were made analytically. In result the detailed tables of the pressure decrement of the heat capacity depending on salinity, temperature and pressure were calculated, which then are approximated by the polynomial

$$Cp(S,t,p) - Cp(S,t,0) = - \sum_0^3 \left[\sum_1^3 \left(\sum_0^4 a_{ijk} t^i \right) p^j \right] S^{k/2}, \quad (4)$$

The coefficients of this equation are found by the least square method, are presented in table 1.

Table 1. The coefficients a_{ijk} of the equation (4)

k	i	$j=1$	$j=2$	$j=3$
0	0	4.9514372808 E+00	-2.3552801045 E-02	5.0640927466 E-05
	1	-1.4263866090 E-01	6.2570700008 E-04	-1.3331605812 E-06
	2	2.6132521024 E-03	1.8924815727 E-05	-9.1927816434 E-08
	3	-1.8178701052 E-07	-1.2973481571 E-06	5.1849426988 E-09
	4	-3.8520988973 E-07	1.7203446399 E-08	-6.6538988706 E-11
1	0	7.1832317316 E-03	-1.5937726748 E-04	5.9823245699 E-08
	1	-7.4689649870 E-03	1.4317090494 E-04	-5.7783085843 E-07
	2	1.1404203950 E-05	-2.1753128716 E-05	9.1153595897 E-08
	3	-4.9271177535 E-05	9.7271320938 E-07	-3.9321489805 E-09
	4	6.4576682563 E-07	-1.3364830637 E-08	5.1691578108 E-11
2	0	-5.4157253265 E-02	3.9202321415 E-04	-4.0916714036 E-07
	1	3.5638576812 E-03	-5.3027204911 E-05	1.5642635996 E-07
	2	-3.0481992352 E-04	5.5216151524 E-06	-2.2284387782 E-08
	3	1.2057899862 E-05	-2.3312426077 E-07	9.4618255255 E-10
	4	-1.5774498925 E-07	3.2207785677 E-09	-1.2457002276 E-11
3	0	1.8100984130 E-03	-2.0973184019 E-05	-2.5469115280 E-08
	1	-1.7861965645 E-04	3.7472351915 E-06	-8.3967364973 E-09
	2	2.1971489314 E-05	-4.1816870896 E-07	1.6472078289 E-09
	3	-9.1124663178 E-07	1.7723777125 E-08	-7.2115500760 E-11
	4	1.1910527144 E-08	-2.4473805428 E-10	9.4656659631 E-13

The equation (4) describes the set of initial computed data with a standard deviation of 0.003 % and applicable in an interval of salinity $0 \leq S \leq 40$, temperature $0 \leq t \leq 40$ °C and at pressure up to 130 MPa. The values of arguments S and t are necessary to use according to PSS-78 and IPTS-68. Check value: $Cp(40,40,130) = 3813.036$ J/(kg·K). The accuracy of heat capacity data, computed by equation (4) is within ± 0.05 % at atmospheric pressure and smoothly increases with increasing of pressure, reaching 0.08 %

at 130 MPa. Since under consideration interval of temperature distinction between temperature scales IPTS-68 and ITS-90 is small, and accuracy of C_p data rather low, the equation (4) can be used for the temperature scale ITS-90. However for more precise calculations it should be given in the scale ITS-90.

Results and discussion. In figure 1 are shown the results of comparison of our data with UNESCO [8] tables. The relative deviations were calculated by formula $d = (C_{p[8]} - C_{p[this\ work]}) / C_{p[this\ work]} \times 100$. From figure 1 it is seen, that the divergences basically are within $\pm 0.05\%$ ($\pm 2\text{ J}/(\text{kg}\cdot\text{K})$). However, it is necessary to notice that over the oceanic range of temperature, salinity and pressure, divergences considerably increase (the data [8] basically are overestimated).

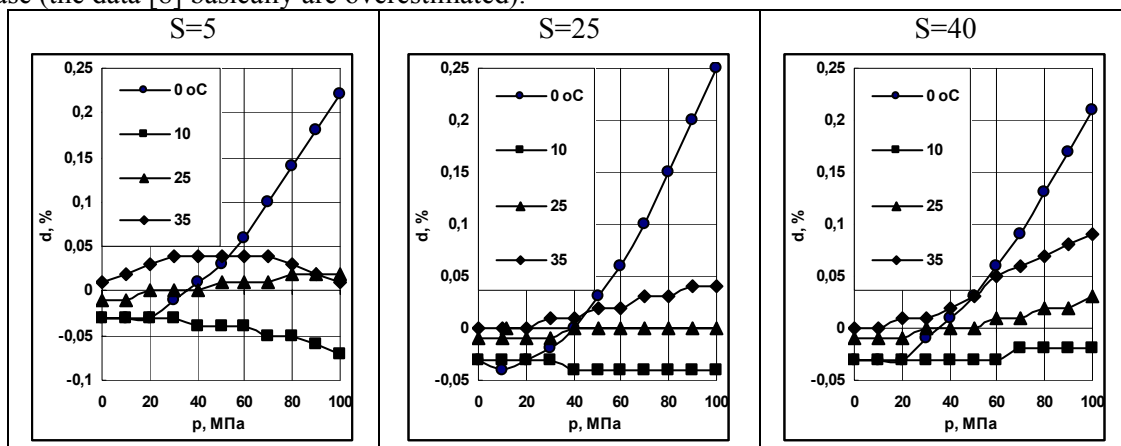


Fig. 1. Deviations of the data of UNESCO [8] from our results

The analysis of the obtained data has shown, that in the investigated region of parameters of states the heat capacity changes over a wide range - from $C_p(0,0,0)=4218.8\text{ J}/(\text{kg}\cdot\text{K})$ up to $C_p(40,0,130)=3708.1\text{ J}/(\text{kg}\cdot\text{K})$, that makes about 12.1 % from initial value. The complex form of the dependence $C_p=C_p(S,t,p)$ evidence of significant structural changes of water under influence of S,t,p -factors. That fact pays attention, that with increasing pressure or salinity the heat capacity changes (decreases) monotonously, while its temperature change in various areas is miscellaneous.

From consideration the fig. 2, in which the isotherms of the pressure decrement of heat capacity are given, it is visible, that the C_p decreases with increasing of pressure and the greatest speed of its decrease falls to an isotherm $0\text{ }^\circ\text{C}$. With increasing of salinity and/or temperature the absolute value of pressure decrement of heat capacity decreases. It is typical also, that with increasing of pressure, temperature or salinity the pressure coefficient of heat capacity (remaining negative) increases, meanwhile the derivative $\partial^2 C_p / \partial p^2$ being positive, on the contrary, decreases.

On fig. 3 the isobars of temperature dependence of heat capacity of SW for salinity 40 are presented. For comparison similar dependence for pure water at atmospheric pressure here is given. Apparently from figure, at low pressure the isobars of $C_p=C_p(t)$ have a minimum ($\partial C_p / \partial t < 0$ at $t < t_{\min}$). This anomaly of water and aqueous solutions is well-known for a long time. According to the equation (3) at atmospheric pressure the coordinate of the minimum are: $t_{\min} = 36.484\text{ }^\circ\text{C}$ and $C_{p,\min} = 4177.778\text{ J}/(\text{kg}\cdot\text{K})$. Anomalies of the heat capacity, as well as anomalies of any other properties of water and aqueous solutions, caused by the polymorphic transformations occurring in liquid water under influence of temperature, pressure or the dissolved substances.

With increasing of pressure and/or addition of salt (increasing of salinity) the structure of water (solvent) gradually changes, the equilibrium is displaced aside more dense structures. It finds the reflection on the temperature dependence of the heat capacity: the minima are deformed, being displaced aside low temperatures and at certain values of S^* and p^* , they degenerate. Inversely proportional dependence between values of S^* and p^* is observed. With decreasing of temperature the S,p -region of anomaly extends. On the basis of available data it is not possible to determine the low temperature borders of anomaly $\partial C_p / \partial t < 0$, as it comes into the supercooled region. For an example we shall present some values of S^* and p^* at temperature $0\text{ }^\circ\text{C}$: $S^*=0, p^*=29.2\text{ MPa}$; $S^*=20, p^*=16.8\text{ MPa}$ and $S^*=40, p^*=4.5\text{ MPa}$.

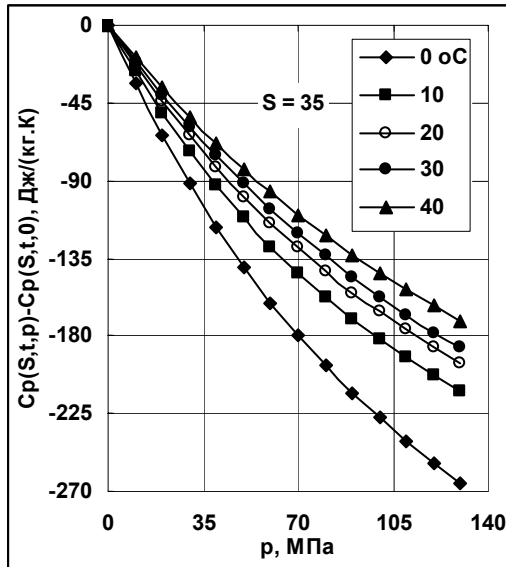


Fig. 2. The pressure decrement of heat capacity at various temperatures versus pressure

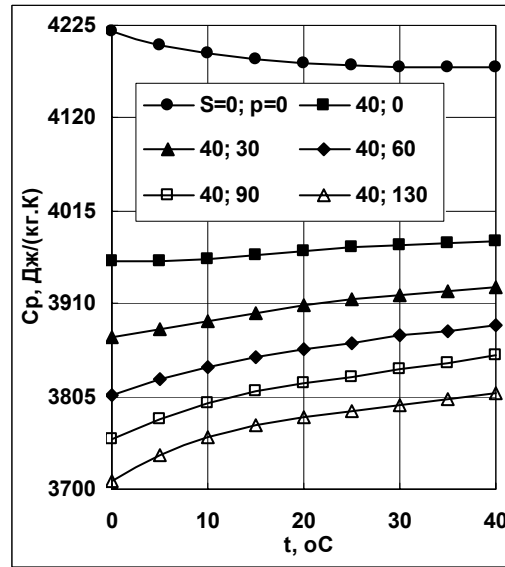


Fig. 3. The temperature dependence of heat capacity at various pressures

Further, the analysis carried out with the help of the equation (4) has shown, that the second derivatives $\partial^2 C_p / \partial t^2$, $\partial^2 C_p / \partial t \partial S$, $\partial^2 C_p / \partial t \partial p$ and derivatives of higher order also have abnormal behavior. We shall note, in particular, that at low temperatures $\partial^2 C_p / \partial t^2 > 0$. The region of this anomaly is much wider than the region where the $\partial C_p / \partial t$ is negative.

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