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Second-order phase transitions in water

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ABSTRACT

Piecewise approximation analysis of experimental data for the isobaric heat capacity Cp = f (T) dependence for water revealed points of the second-order phase transition (PT2). In the temperature range of 273K – 373K (0^0C - 100^0Ñ) there were found five such points and the temperature values initiating the PT2 were calculated. The validity of determining the critical points is corroborated by the published experimental data on anomalous properties of water at these points.

KEYWORDS

Water;
Second-order phase transition;
Critical points;
Temperature;
Approximation.

INTRODUCTION

Phase transitions are a natural phenomenon that is they are an objective reality observable in natural conditions. The first-order phase transition is quite an ordinary thing and can be observed by the naked eye: when it is raining, it is condensation[1]; when it is snowing, it is crystallization; when the rain-wet asphalt road is gradually getting dry, it is evaporation. It is much more difficult to watch the second-order phase transition, which is a structural rearrangement of the system. This transition is not so apparent, however it has far-reaching consequences. The striking difference in the properties between diamond and graphite is determined by the differences in their structure that is in their lattice structure. However, to cause structural rearrangements in carbon is a very difficult problem, both theoretically and practically. Both superfluidity and superconductivity are known to occur as a result of the second-order phase transition, though initiating such a transition is also a difficult scientific and technical problem.

Phase transitions can be observed while controlling heat capacity or entropy. The entropy is a function of the system's thermodynamic state reflecting its structure and relative positioning of interacting particles. The function's value is determined by the set of values of system-affecting factors, such as temperature, pressure, chemical potential, electrical field intensity, magnetic field induction, and so on. As soon as at least one system-affecting factor's value reaches a certain level there takes place a PT2, and the structure of the system changes[2].

The starting point for the second-order phase transition theory worked out by L. D. Landau is the copresence of at least two structures within the system[3].

Today, more than forty variants of water structure have been theoretically substantiated and experimentally supported. The PT2 points are most easily determined by the anomalous run of the isobaric heat capacity function of a changeable factor, for instance, temperature[4].

If the system comprises only two structures the heat capacity function of the changeable factor has a well pronounced extremum due to which the PT2 point, because of a close similarity of the function graph's shape to the Greek letter "λ", is called lambda-point. But if within the system there coexist several structures distinct extremums may not be observed since heat capacity of each structure can vary according to its individual law, and the system's heat capacity measured in the experiment would represent only the superposition of heat capacities of individual structures. In this case the observed (measured) function may not have clearly pronounced extremums, but it will comprise "singular points", that is the function's inflection points.

The data on localization of "singular points" can be useful to researchers of thermodynamic properties of water and water solutions by development of methods preparation, to thermal engineers at calculation of thermophysical properties of water.

SEARCH OF THE SINGULAR POINTS

To locate the singular points in the curve of water isobaric heats capacity function of temperature we used the method of piecewise approximation of experimental data borrowed from reference sources[5]. The search technique was as follows: in a temperature interval a group of three heat capacity values were taken and the approximate equation was selected. For this purpose we used a program that automatically selected "the best" of the thirty-six approximate equations. Then a 0.1^{0}C step was made and a point was added, and the approximate equation was again selected. At each step an equation was selected for which the Index of multiple determination[6] R^2 proved to be maximal, and the dispersion s^2 proved to be minimal. The processing was stopped when adding a new point to the date file impaired the statistical findings for the approximate model.

The analysis helped to obtain five equations listed in TABLE 1 (where heat capacity is given in kJ/(kg·K), and temperature is given in Kelvin units).

Figure 1 shows heat capacity-temperature diagram in a range of temperatures from 273K to 373K.

The singular points were found by joint solving of the equations for the adjoining temperature spans. The critical points found and the temperature intervals between those points are listed in TABLE 2.

TABLE 1 : Analytical representation of isobaric heat capacity of water as a function of temperature in the range of 273K to 373K

№№	C_p = f (T)	Multiple Correlation coefficient, R^2	Root-mean-square deviation, ±s,kJ/(kg·K)
1.	$C_p = T^2/(-21806 + 144.60 \cdot T)$	0.99988	0.00010
2.	$C_p = T^2/(-21262 + 142.64 \cdot T)$	0.99996	0.00004
3.	$C_p = (470.97/T) \cdot \exp(3.2633 \cdot 10^{-3} \cdot T)$	0.99978	0.00023
4.	$C_p = 1/(0.24309 - 1.2028 \cdot 10^{-5} \cdot T)$	0.99770	0.00029
5.	$Cp = 1/(0.25009 - 3.3226 \cdot 10^{-5} \cdot T)$	0.99972	0.00028
6.	$Cp = (516.48/T) \cdot \exp(2.9849 \cdot 10^{-3} \cdot T)$	0.99997	0.00013

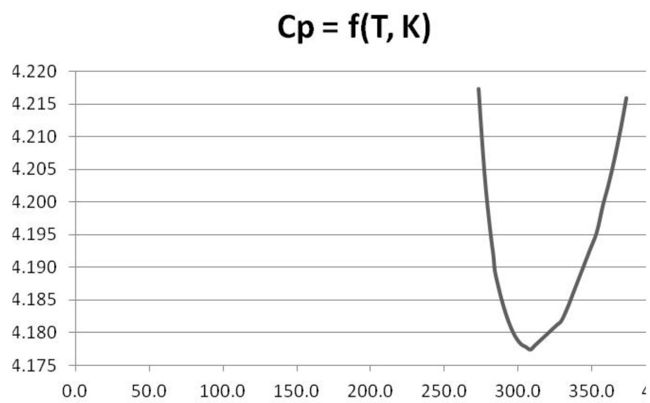

Figure 1 : Change of water isobar heat capacity building-up temperature

TABLE 2 : Critical points for water in the temperature range of 273 to 373 K

Span №№	Temperature interval, K	Critical point ordinate, (K)	Critical point ordinate, (^{0}C)
1	273 – 278		
2	278 - 287	277.32	4.17
2	278 - 287		
3	287 – 307	286.48	13.33
3	287 – 307		
4	307 – 330	306.10	32.95
4	307 – 330		
5	330 – 345	329.80	56.65
5	330 – 345		
6	345 - 372	343.16	70.01

Thus piecewise approximation of the Cp = f (T) function helped to reveal the inflection points. There were also found the critical points at which there takes place a restructuring of the system, i.e. the second-order phase transition. Since at these points physicochemical (thermophysical) properties of the system undergo changes, it can be helpful to recall what we know about the anomalous points of water properties.

Repeated experimental research helped to establish certain particular areas of anomalous changes in water properties while changing the water's temperature. At around 4^0C water has maximal density and minimal heat capacity at around 34.5^0C[7].

Some researchers found the minimums of isothermal[8,9] and adiabatic[10] compressibility in the temperature range of 30^0 to 35^0C, and minimal heat capacity and viscosity at around 30^0C[11].

Particular points of magnetic relaxation for water protons were found at the temperatures of 15^0C, 30^0 to 35^0, 40^0 to 45^0, and 60^0C[12]. Anomalous points of refraction and electronic polarizability were found at the temperatures 55^0C to 57^0C[13].

CONCLUSIONS

1. The second-order phase transition (PT2) takes place in nature at a definite set of values of the factors that determine thermodynamic state of the system, such as temperature, pressure, chemical potential, electrical field intensity, magnetic field induction, etc.
2. With two structures co-present within the system the transition from one structure to the other (PT2) is manifested as an extremum in the curve of the entropy (heat capacity, evaporation heat) function of the factor value, that is as λ-point.
3. In associated liquids, where water belongs, there can coexist more than two structures, therefore in the curve function of the thermodynamic state extremums may not be observed, but instead there can be observed singular points, or the function inflections.
4. Piecewise approximation analysis of the published experimental data for the function of water isobaric heat capacity of temperature in the temperature range of 0^0 to 100^0C (273K to 373K) helped to reveal five singular points at the temperatures of 4.2^0, 13.3^0, 32.9^0, 56.7^0 and 70.0^0C. We interpret these points as PT2 that is structural rearrangement in water.
5. A lot of researchers observed certain singular properties of water at the temperatures of 4^0, 15^0, 30^0 to 35^0, 40^0 to 45^0 and 60^0C.
6. Some indistinctness as regards the PT2 temperatures for water can be accounted for by at least three reasons:

   - there has been observed a certain superpositioning of heat capacities of individual structural fractions (clusters), whose size-distribution function is not constant;
   - under natural conditions water is an open dynamical system whose state is uncontrollably affected by various factors, such as electromagnetic radiation, the magnetic field of the Earth and the gravitational field; and
   - the method of measurement employed affects the cluster structure of water.

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