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The effect of undissolved air on isochoric freezing

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ABSTRACT

This study evaluates the effect of undissolved air on isochoric freezing of aqueous solutions. Isochoric freezing is concerned with freezing in a constant volume thermodynamic system. A possible advantage of the process is that it substantially reduces the percentage of ice in the system at every subzero temperature, relative to atmospheric freezing. At the pressures generated by isochoric freezing, or high pressure isobaric freezing, air cannot be considered an incompressible substance and the presence of undissolved air substantially increases the amount of ice that forms at any subfreezing temperature. This effect is measurable at air volumes as low as 1%. Therefore eliminating the undissolved air, or any separate gaseous phase, from the system is essential for retaining the properties of isochoric freezing.

1. Introduction

Lowering the temperature reduces the rate of biochemical processes [1]. Therefore, it is used for improving the long term preservation of biological materials in medicine, biotechnology and the food industry. It would be desirable to preserve the biological materials at the lowest temperature possible to reduce the rate of the chemical reactions. However, biological substances are mostly water. Once brought to temperatures below freezing, the water will freeze with a detrimental outcome. The detrimental effects are directly, or indirectly, related to the amount of ice in the system [5,8]. Reducing the amount of ice at any subzero freezing temperature, can improve survival. Our theoretical and experimental studies of isochoric freezing have shown that isochoric freezing can substantially reduce the amount of ice in the system, relatively to an atmospheric isobaric system, at the same temperature [7,9,10].

While performing the experiments reported in Refs. [7,9,10], we observed that the presence of undissolved air in the system can have a profound effect on isochoric freezing. The goal of this study is to quantify the effect of undissolved gasses (air), on isochoric freezing. The study consists of a theoretical analysis with experimental validation. The analysis shows that even very small amounts of undissolved air in an isochoric system can completely change the expected outcome of the process. It should be emphasized that these findings are also relevant to high pressure isobaric freezing.

2. Materials and methods

2.1. Thermodynamic analysis

In a pure substance the phase change temperature and pressure are dependent thermodynamic properties. The relation between temperature and pressure for ice and water in thermodynamic equilibrium is well known. The water-ice I region is shown in Fig. 1 (after [3]). The minimum temperature in which liquid water can coexist with ice I, is − 21.985 °C at a pressure of 209.9 MPa.

In order to simplify the calculations a curve relating temperature (°C) and pressure (MPa) was generated with the data obtain from Kalichevsky [4].

$$P = -0.1461T^2 - 12.58T + 0.1013 \quad (1)$$

In the case of aqueous solutions, both the concentration of solute and the pressure affect the phase change temperature. Following the method of our previous analysis [7,9,10] we assume that their effect is a linear superposition, given by Equation (2):

$$T_{ph} = \Delta T(P) + \Delta T(c), \quad (2)$$

where the first term in the right hand side of Equation (2) represents the change in freezing temperature due to the pressure and the second term represents the effect of concentration. For this particular study we analyzed the isochoric freezing in a physiological solution of sodium chloride (NaCl). For this solution, the

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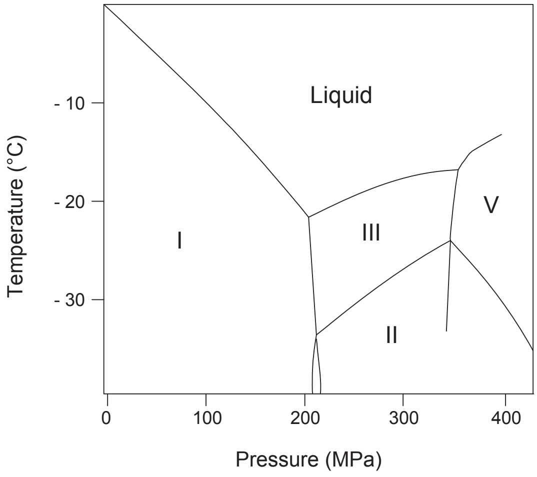

Fig. 1. Phase diagram of water near to ice I region.

effect of pressure and concentration on phase change temperature can be represented by Equations (3.a) and (3.b) as follows:

$$\Delta T(P) = -4 \times 10^{-10}P^3 - 3 \times 10^{-7}P^2 - 0.00809P + 0.00812 \tag{3.a}$$

$$\Delta T(c) = -294.15 \cdot c^3 - 80.193 \cdot c^2 - 54.402 \cdot c \tag{3.b}$$

Equation (3.a) was taken from Kalichevsky [4], and Equation (3.b) from Ref. [2].

One of the most important relations for the analysis of the isochoric process of freezing process is the quality, Z, which represents the mass fraction of water in the ice-water mixture inside a vessel at a specific phase change temperature. Equation (4) is a mathematical definition of the quality:

$$Z = \frac{v_0 - v_1}{v_2 - v_1} \tag{4}$$

The subscript 0 represents the initial specific volume of the system, and subscripts 1 and 2 represent the specific volumes of ice and water at a particular phase change temperature. The quality of this mixture can be calculated by knowing other specific properties such as the internal energy, the enthalpy, etc., for the all states. The approach for this problem is very similar to the one develop in Refs. [7,9,10].

The calculations for specific volumes of ice and water as published by Nagornov and Chizhov [6] are based on the compressibility and the thermal expansion coefficients. They can be obtained by doing a first order Taylor expansion on the volume with respect to pressure and temperature.

$$dv = \frac{\partial v}{\partial P}dP + \frac{\partial v}{\partial T}dT$$

By definition the compressibility (β) and thermal expansion (α) are:

$$\beta = \frac{1}{v}\frac{\partial v}{\partial P} \text{ and } \alpha = \frac{1}{v}\frac{\partial v}{\partial T}$$

Equations (5) and (8) are obtained by substituting the compressibility and the thermal expansion coefficients in the partial derivatives.

2.1.1. For ice

$$v_1 = v_{10}\exp\left[-\int_{P_o}^{P}\beta_{T1}(P',T)dP' + \int_{T_0}^{T}\alpha_{T1}(P_o,T')dT'\right] \tag{5}$$

Here β and α are the compressibility coefficient and the coefficient of thermal expansion respectively. Again the subscript 1 is for the ice and the subscript 0 represents the properties at the phase change at 0 °C and 1 atm. In a similar fashion subscript 10 represents the property of ice at 0 °C and 1 atm.

$$\alpha_{T1}(P_o,T) = A_1 + A_2T + A_3T^2 + A_4T^3 \tag{6}$$

$$\beta_{T1}(P,T) = \frac{\beta_{T1}^0}{1 + m_1\beta_{T1}^0P}; \quad \beta_{T1}^0 = \frac{\beta_1}{1 - \beta_2T}, \tag{7}$$

where $A_1 = 1.5756 \cdot 10^{-4}$, $A_2 = 5.556 \cdot 10^{-7}$, $A_3 = 2.655 \cdot 10^{-8}$, $A_4 = 7.11 \cdot 10^{-10}$, $\beta_1 = 1.827 \cdot 10^5$, $\beta_2 = 1.418 \cdot 10^{-3}$. The specific volume for ice can be calculated numerically by substituting the coefficients derived from (6) and (7) into Equation (5). The units of pressure and the temperature for these correlation units are in centigrade are in bars and centigrade.

2.1.2. For water

The specific volume of water is given by Equation (8).

$$v_2 = v_{20}\exp\left[-\int_{P_o}^{P}\beta_{T2}(P',T)dP' + \int_{T_{k0}}^{T_k}\alpha_{T2}(P_o,T')dT'\right] \tag{8}$$

The compressibility and thermal expansion coefficients are:

$$\beta_{T2}(P,T) = \left(\sum_{i=1}^{4} b_iP^i\right) \times 10^{-4} \tag{9}$$

$$\alpha_{T2} = \left(A + \frac{B}{C + \Gamma}\right) \times 10^{-4} \tag{10}$$

In Equation (10) A, B, C and Γ are functions of temperature and pressure expressed:

$$\begin{aligned} A &= a_1 + a_2T_K + a_3T_K^2 \\ B &= a_4 + a_5T_K + a_6T_K^2 + a_7T_K\Gamma + a_8\Gamma \\ C &= a_8 + a_9T_K + a_{10}T_K^2 + a_{11}T_K^3 \\ \Gamma &= P + a_{13}P^2 + a_{14}P^3 \end{aligned} \tag{11}$$

The units of pressure and temperature for these correlations are in bars and Kelvin. The specific volume of water can be calculated numerically using constants from Ref. [3]:

$a_1 = 4.78506 \times 10^{1}$
$a_2 = -8.12847 \times 10^{-2}$
$a_3 = 8.49849 \times 10^{-5}$
$a_4 = 5.56047 \times 10^{5}$
$a_5 = -3.76355 \times 10^{3}$
$a_6 = 5.56395$
$a_7 = 5.59682 \times 10^{-3}$

$a_8 = -2.76522 \times 10^{1}$
$a_9 = -4.28067 \times 10^{3}$
$a_{10} = -3.39150 \times 10^{1}$
$a_{11} = 3.65873 \times 10^{-1}$
$a_{12} = -5.89617 \times 10^{-4}$
$a_{13} = 3.28892 \times 10^{-4}$
$a_{14} = 2.65933 \times 10^{-8}$

and