A Description of the Melting of Ice With the Modified Clapeyron–Clausius Equation

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Abstract

Previously, the author found that the traditional Clapeyron–Clausius equation fails to describe the phase transitions in substances with negative thermal expansion. A modified Clapeyron–Clausius equation was therefore proposed, which described these transitions very well. However, this modified equation failed to describe the melting of ice. It is shown here that the modified Clapeyron–Clausius equation describes the melting of ice successfully if the compressibility of water and ice is considered.

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Running title: A description of the melting of ice

Keywords. Phase diagrams; phase transformations; phase transitions; phase equilibria; water; ice.

1. Introduction

In [1][2][3], it was shown that the traditional Clapeyron–Clausius equation produces significant errors when used to describe the phase transitions in ice, iodine and some other substances with negative thermal expansion. A modified Clapeyron–Clausius equation was then proposed, that took the sign of thermal expansion into account, and which described most of these transitions reliably, as follows:

$$\frac{dT}{dP} = \frac{T\left(\mathrm{sign}\alpha_2 V_2 - \mathrm{sign}\alpha_1 V_1\right)}{\Delta H}$$

Where ΔH is the change in the enthalpy, V_i are the volumes of the both phases, and α_1 and α_2 are the thermal expansion coefficients of the two phases. Here it is necessary to mention the work in [4], where the slopes dT/dP were obtained experimentally. However, this equation failed to describe the melting of ice [2][3], whereas the traditional Clapeyron-Clausius equation, equation (2):

$$\frac{dT}{dP} = \frac{T\left(V_2 - V_1\right)}{\Delta H}$$

gives the correct result, with the slope of the melting curve equal to -0.074KMPa^{-1}. (It is widely assumed that α_1 is positive at the melting temperature, and α_2 is negative at the same temperature. In this case, equation (1) gives the slope as -1.71 K MPa^{-1}.

According to many sources, the thermal expansion coefficient of ice at $T = 0°C$ and $P = 1$ atm is positive and the thermal expansion coefficient of water is negative [5]. Nevertheless, a negative value of the thermal expansion coefficient of ice at $T = 0°C$ is reported in a basic Chemical Encyclopedia[6]: as $\alpha_1 = -1.2 \cdot 10^{-4}\,°C^{-1}$ With this value for α_1 and a negative α_2 dT/dP calculated with equation (1) will be positive and equal in absolute value to that calculated using equation (2):

$$dT/dP = 0.074 \text{K MPa}^{-1}.$$

2. Theoretical considerations

It is, therefore, necessary to rederive equation (1) to take into account the compressibilities of the substances, which leads to the following equation (4) [7]:

$$\frac{dT}{dP} = \frac{T\left(\text{sign}\alpha_2 \beta_2 V_2 - \text{sign}\alpha_1 \beta_1 V_1\right)}{\Delta H}$$

where β_i are the compressibilities of both phases: (here, index 1 refers to ice, and index 2 refers to water).

The other values for ice and water at $T = 273.15$ K are: $\rho_1 = 0.917$ g cm^{-3}, $\rho_2 = 0.99987$ g cm^{-3}, $\alpha_2 = -3.4 \cdot 10^{-5}\,°C^{-1}$ and $\Delta H = 5.99$ kJ mol^{-1} [6].

In [3][8][9][10], it was shown that the isothermal compressibilities of water and ice at 0°C must be negative, and the authors of [11][12] reported that water could have negative compressibility. In[13], the isothermal compressibility of water at 0°C was measured and found to be negative, meaning that the volume increases under pressure:

$$\Delta V = aP + bP^2,$$

where log $a = 5.5942 - 10$, and log($-b$) = 1.3512 -10.

In [12], the isothermal compressibility of ice I at 0 °C was computed and found to be negative, and in[13], the compressibility of ice VI above 0 °C was also directly measured and found to be negative. It is noteworthy that

Bridgman [13] used his own definition of compressibility as follows:

$$\beta = \left(\frac{\frac{\partial V}{\partial P}}{}\right)_T .$$

3. Conclusions

There are a number of studies in which negative values for the compressibility of ice and water were found experimentally. The modified Clapeyron-Clausius equation: equation (3) takes this result into account, and describes the melting of ice very well. Further investigation of the applicability of this equation to other substances is necessary.

In [14] experimental data for water were presented which confirm that water has negative compressibility: Table 1.

Table 1. Density of water at T =273.16K and different pressures

No	P, Mpa	ρ, Kg m^{-3}	β Pa^{-1}
1	0	999.87	- 1.259100E-07
2	0.000612	999.793	4.854740E-10
3	0.05	999.817	- 1.061570E-09
4	0.1	999.843	–2.700484E-10
5	P=0.101325	999.843	–2.665171E-10

The compressibilities in Table 1 are calculated by the following equation (7):

$$\beta_i = -\frac{V_2 - V_1}{V_1\left(P_2 - P_1\right)} .$$

Here index i varies from 1 to 5. For i =1, P_1 =0 and P_2 =0.000612. For i =2, P_1 =0.000612 and P_2 =0.05. For i =3, P_1 =0 and P_2 =0.05.

For i =4, P_1 =0 and P_2 =0.1, For i =5, P_1 =0 and P_2 =0.101325.

Statements and Declarations

Competing Interests

The author has no competing interests to declare that are relevant to the content of this article.

Data Availability

The data that support the findings of this study are available from the author, upon reasonable request.

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