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On taking into account the irreversibility of first-order phase transitions

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Based on the fact of irreversibility of the real first-order phase transition (PT-1), an inequality was obtained that generalizes the Clapeyron–Clausius equation (CCE) in the case of irreversibility of PT-1: the Clapeyron–Clausius inequality. It was shown that the CCE determines only the maximum possible slope of the line PT-1 in the coordinates temperature–pressure and temperature–intensity of an external homogeneous magnetic (or electric) field. Analysis of experimental data for various types of PT-1 has shown that the deviation from the CCE is more noticeable the more jump in volume or jump in magnetization (or polarization) at PT-1.

Keywords: first-order phase transition, Clapeyron–Clausius equation, irreversibility, magnetic field.

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1. Introduction

It is known that a first-order phase transition (PT-1) is characterized by an abrupt change in volume (ΔV_m) and a release or absorption of latent heat (ΔQ_m) of PT-1 at a constant temperature (T_m) and pressure (P) of PT-1. The Clausius–Clapeyron equation (CCE) establishes a relationship between the ratio of the jump in volume to the latent heat of PT-1 and the slope of the PT-1 line in temperature–pressure coordinates (dT_m/dP) in the following form [1–6]:

$$\frac{dT_m}{dP} = T_m \frac{\Delta V_m}{\Delta Q_m} = \frac{\Delta V_m}{\Delta S_m}. \quad (1)$$

Here ΔS_m is change in entropy during PT-1, for which the equality of the following form is assumed to be satisfied when deriving (1):

$$\Delta S_m = \frac{\Delta Q_m}{T_m}. \quad (2)$$

In the presence of a homogeneous magnetic (or electric) field of strength H , the temperature of PT-1 can change due to a change in H . In this case, the CCE takes the following form [7–10]:

$$\left(\frac{dT_m}{dH}\right)_P = -\frac{\Delta M_m}{\Delta S_m} = -T_m \frac{\Delta M_m}{\Delta Q_m}, \quad (3)$$

where M is magnetization (or polarization in the case of electric field) for a given phase of the substance.

However, during the experimental study of PT-1, a deviation of formula (1) from the experimental data was noticed in [2–6], and a deviation of formula (3) was noticed in [9,10]. The question arises: why do (1) and (3) poorly describe the relationship of experimental data for PT-1? This study is devoted to answering this question.

2. The Clausius–Clapeyron inequality

According to the second law of thermodynamics [1], the amount of heat (dQ) received by the system from a thermostat with temperature T results in a change in entropy (dS) of the system, and in the general case the following condition must be satisfied:

$$dQ \leq TdS. \quad (4)$$

The equal sign in (4) is satisfied only if the process of transition of the system from a state with entropy S to a state with entropy $S + dS$ is reversible. Reversible is a process when the system can be passed in the forward and reverse directions through a sequence of the same thermodynamic states [1,11]. It is clear that the reversible process is an idealization [11]. It is easy to understand that real PT-1 is an irreversible process. This is a conclusion made from the following experimental facts.

1. During PT-1 at a certain temperature (T_m) and pressure (P_m), the entropy of the system changes by a noticeable amount (ΔS_m), which, in the general case, cannot be considered infinitely small [2–10,12].

2. The PT-1 process in the forward and reverse directions, in the general case, does not pass through a sequence of the same thermodynamic states. A real PT-1 always has a hysteretic behavior [12–17].

For example, having melted a crystal isobarically at T_m , upon subsequent cooling the liquid will begin to crystallize (or amorphize), as a rule, at a temperature lower than the melting point [12–17]. Following the [11], it can be said that during melting, the information about the system is erased and converted into entropy. Therefore, PT-1 is, in the general case, an irreversible process. In this context, the question arises: how will taking into account the irreversibility of PT-1 change the CCE in the form of (1)

and (3), which are obtained on the basis of the postulate of PT-1 reversibility?

In the equilibrium coexistence of two macroscopic phases during PT-1, the following equilibrium conditions must be observed [1]: $P_1 = P_2 = P_m$ is mechanical, $T_1 = T_2 = T_m$ is thermal, and $\mu_1 = \mu_2$ is chemical equilibrium conditions. Here μ is chemical potential. It should be clarified that the kinetics of PT-1 is not considered here. Here the static coexistence of two macroscopic phases is considered.

Thus, in the presence of a homogeneous magnetic (or electric) field of strength H the following condition should be satisfied on the PT-1 line [1, Ch. 4]:

$$\Delta\mu = \mu_2 - \mu_1 = 0,$$

$$\left(\frac{\partial\Delta\mu}{\partial T}\right)_{P,H} \neq 0, \quad \left(\frac{\partial\Delta\mu}{\partial P}\right)_{T,H} \neq 0, \quad \left(\frac{\partial\Delta\mu}{\partial H}\right)_{T,P} \neq 0.$$

From these expressions the following equality can be derived:

$$d\Delta\mu = \left(\frac{\partial\Delta\mu}{\partial T}\right)_{P,H} dT + \left(\frac{\partial\Delta\mu}{\partial P}\right)_{T,H} dP + \left(\frac{\partial\Delta\mu}{\partial H}\right)_{T,P} dH = 0. \quad (5)$$

Hence, for $H = \text{const}$ we get

$$-\left(\frac{\partial\Delta\mu}{\partial T}\right)_{P,H} dT = \left(\frac{\partial\Delta\mu}{\partial P}\right)_{T,H} dP. \quad (6)$$

From (5) with $P = \text{const}$ we get

$$-\left(\frac{\partial\Delta\mu}{\partial T}\right)_{P,H} dT = \left(\frac{\partial\Delta\mu}{\partial H}\right)_{T,P} dH. \quad (7)$$

For $T = \text{const}$ from (5) we get

$$-\left(\frac{\partial\Delta\mu}{\partial P}\right)_{T,H} dP = \left(\frac{\partial\Delta\mu}{\partial H}\right)_{T,P} dH. \quad (8)$$

For an irreversible process, according to (4), the following should be true:

$$TdS \geq dU + PdV - HdM, \quad (9)$$

where M is magnetization (or polarization in the case of electric field) for the given phase of the substance, U is internal energy, which is related to the chemical potential of the system from N particles by the following equality [1]:

$$N\mu = U - TS + PV - MH.$$

Hence, for $N = \text{const}$ we get

$$d\mu = \frac{dU}{N} - T \frac{dS}{N} - \frac{S}{N} dT + P \frac{dV}{N} + \frac{V}{N} dP - \frac{M}{N} dH - H \frac{dM}{N}.$$

From this equality, using (9), for an irreversible process we get

$$d\mu \leq -\frac{S}{N} dT + \frac{V}{N} dP - \frac{M}{N} dH. \quad (10)$$

From (10) for an irreversible process it is easy to obtain the following expressions:

$$\frac{S}{N} \leq -\left(\frac{\partial\mu}{\partial T}\right)_{P,H}, \quad \frac{V}{N} \geq \left(\frac{\partial\mu}{\partial P}\right)_{T,H}, \quad \frac{M}{N} \leq -\left(\frac{\partial\mu}{\partial H}\right)_{P,T}.$$

The equal sign in these expressions is valid only for a reversible process. At the same time, these expressions are transformed into well-known equalities [1].

Due to the fact that the $\Delta\mu$ function describes PT-1, i. e. an irreversible process, which was not taken into account in the derivation of the CCE, then the following relationship can be obtained for this function:

$$d\Delta\mu \leq -\frac{\Delta S_m}{N} dT + \frac{\Delta V_m}{N} dP - \frac{\Delta M_m}{N} dH = 0. \quad (11)$$

From (11) with $H = \text{const}$, it is easy to obtain two inequalities

$$\begin{aligned} \left(\frac{\Delta S_m}{N}\right) dT &\leq -\left(\frac{\partial\Delta\mu}{\partial T}\right)_{P,H} dT, \\ \left(\frac{\partial\Delta\mu}{\partial P}\right)_{T,H} dP &\leq \left(\frac{\Delta V_m}{N}\right) dP. \end{aligned}$$

Hence, taking into account (6), we get

$$\begin{aligned} \left(\frac{\Delta S_m}{N}\right) dT &\leq -\left(\frac{\partial\Delta\mu}{\partial T}\right)_{P,H} dT \\ &= \left(\frac{\partial\Delta\mu}{\partial P}\right)_{T,H} dP \leq \left(\frac{\Delta V_m}{N}\right) dP. \end{aligned} \quad (12)$$

Similarly, for $P = \text{const}$ from (11) and (7) we get

$$\begin{aligned} \left(\frac{\Delta S_m}{N}\right) dT &\leq -\left(\frac{\partial\Delta\mu}{\partial T}\right)_{P,H} dT \\ &= \left(\frac{\partial\Delta\mu}{\partial H}\right)_{T,P} dH \leq -\left(\frac{\Delta M_m}{N}\right) dH. \end{aligned} \quad (13)$$

For $T = \text{const}$ from (11) and (8) we get

$$\begin{aligned} -\left(\frac{\Delta V_m}{N}\right) dP &\leq -\left(\frac{\partial\Delta\mu}{\partial P}\right)_{T,H} dP \\ &= \left(\frac{\partial\Delta\mu}{\partial H}\right)_{T,P} dH \leq -\left(\frac{\Delta M_m}{N}\right) dH. \end{aligned} \quad (14)$$

From (12) we get an inequality that generalizes CCE (1) to the case of irreversible PT-1 in the following form:

$$\left(\frac{dT_m}{dP}\right)_H \leq \frac{\Delta V_m}{\Delta S_m} \leq T_m \frac{\Delta V_m}{\Delta Q_m}. \quad (15)$$

From (13) we get an inequality that generalizes CCE (3) to the case of irreversible PT-1 in the following form:

$$\left(\frac{dT_m}{dH}\right)_P \leq -\frac{\Delta M_m}{\Delta S_m} \leq -T_m \frac{\Delta M_m}{\Delta Q_m}. \quad (16)$$

From (14) the inequality for the change in pressure of PT-1 (P_m) with an isothermal change in the strength of a homogeneous magnetic (or electric) field with irreversible PT-1 can be derived:

$$\left(\frac{dP_m}{dH}\right)_T \geq \frac{\Delta M_m}{\Delta V_m}. \quad (17)$$

However, in experiments they do not measure the entropy jump during PT-1, but the latent heat of PT-1, i.e. ΔQ_m . In this case, according to (4), for a process of general type, not equality (2), but an inequality of the following form should be satisfied:

$$\Delta Q_m \leq T_m \Delta S_m. \quad (18)$$

Inequality (18) should further strengthen inequalities (15) and (16) when substituting experimentally measured quantities into them: dT_m/dP , ΔV_m , dT_m/dH , ΔM_m and ΔQ_m . The use of the equal sign in (15)–(18) is permissible only in the limit of reversibility of PT-1, i.e. when the system can be passed in the forward and reverse directions through a sequence of the same thermodynamic states, i.e. under the following conditions:

for the case $H = \text{const}$: $\Delta V_m \rightarrow 0$ and $\Delta S_m \rightarrow 0$
by $\Delta V_m/\Delta S_m = \text{const}$,

for the case $P = \text{const}$: $\Delta M_m \rightarrow 0$ and $\Delta S_m \rightarrow 0$
by $\Delta M_m/\Delta S_m = \text{const}$,

for the case $T = \text{const}$: $\Delta V_m \rightarrow 0$ and $\Delta M_m \rightarrow 0$
by $\Delta V_m/\Delta M_m = \text{const}$. (19)

In this case, expressions (15) and (16) are transformed into the well-known CCE (1) and (3). Earlier in [18], we have obtained the derivation of inequality (15) in a slightly different way. It was also shown there that inequality (15) is clearly manifested in the experimental study of PT-1 transitions where a noticeable jump in volume takes place:

at melting of inert gas crystals:

$$\Delta V_m/V_s = 11\text{--}12\%,$$

at melting of alkaline-halide crystals:

$$\Delta V_m/V_s = 10.5 \text{ (CsCl)} - 29.4 \text{ (LiF)\%},$$

at PT-1 of the liquid–gas type.

It should be noted that in [19] a generalization of the CCE was proposed for the case of PT-1, which has a region of coexistence of two phases $\alpha + \beta$, i.e. it has a region of PT-1 hysteresis. The authors of [19] have pointed out the solidus–liquidus region for a two-component substitution alloy as an example of such a region. To describe this region of PT-1 hysteresis, the authors of [19] have introduced additional degrees of freedom: the dependence of the magnetic field at the boundaries of the hysteresis region (H^α and H^β) on the magnitude of the external magnetic field. Thus, in [19]

for a magnetic system a generalization of the CCE of the following form was obtained [19, Eq. (8)]:

$$-(S^\alpha - S^\beta) \frac{dT}{dH} = M^\beta \frac{dH^\beta}{dH} - M^\alpha \frac{dH^\alpha}{dH}.$$

However, in the presence of PT-1 hysteresis, it is necessary to recognize the irreversibility of this PT-1 as well. Therefore, it is not entirely correct to apply the formulae of reversible thermodynamics to such a PT-1. In addition, the additional degrees of freedom introduced in [19] are determined in the experiment with a large error, which makes it difficult to use this method. For example, in [20] the change in entropy of single-crystal terbium (Tb) in a magnetic field was studied. Using experimental data on heat capacity and magnetostriction, as well as the method from [19], in [20] the change in entropy has been estimated during a complex magnetostructural transition in Tb. However, the obtained value (0.7 J/(kg · K)) turned out to be 40% greater than the value obtained from the magnetization data (0.5 J/(kg · K)). The results from [19,20] also indicate a violation of the CCE as applied to magnetic systems.

Thus, the violation of CCE (1) and (3) noted in the above works is a consequence of the irreversibility of various types of PT-1 investigated in these studies. The irreversibility of PT-1 is also confirmed by the effect of phase transition radiation (PTR) observed during PT-1 [21–25]. Its essence is that during the condensation or crystallization of certain substances (water, metals, and especially noticeably in alkali halide crystals) a bright flash of infrared radiation is observed. As noted in [22], the presence of this PTR is not taken into account by any theory of PT-1. Meanwhile, the energy of the radiation flash can be comparable to the latent heat of PT-1. It is easy to understand that for those substances where the PTR effect is detected, the PT-1 process in the forward and reverse directions does not pass through a sequence of the same states. In this context, it is of interest to use the experimentally detected deviation from CCE (1) as a thermodynamic indication of the PTR presence at PT-1. It can be assumed that during PT-1, in which a deviation from CCE (1) was detected, the PTR should be observed.

It should be noted that the Ehrenfest equations obtained from CCE (1), which describe the second-order phase transition (PT-2) [1], can be easily derived from inequality (15). In this case, it is necessary to take into account that PT-2 is always a reversible process, i.e. conditions (19) are always satisfied at PT-2.

3. Conclusions

1. The Clausius–Clapeyron equation (CCE) is generalized to the case of irreversibility under PT-1: the Clausius–Clapeyron inequality. This inequality is transformed to the CCE only in the case of a reversible PT-1.

2. Based on the fact of the irreversibility of real PT-1s, it is shown that the CCE determines only the maximum possible slope of the PT-1 line in the coordinates of temperature–pressure or temperature–strength of an external homogeneous magnetic (or electric) field.

3. The analysis of experimental data for various types of PT-1 has shown that the deviation from the CCE is more noticeable, the larger is the jump in volume or the jump in magnetization (or polarization in the case of electric field) at PT-1.

4. It is indicated that deviations of experimental data from CCE (1) correlate with the effect of the presence of phase transition radiation at PT-1. This makes it possible to use the magnitude of the deviation from CCE (1) for thermodynamic indication of the probability of observing the phase transition radiation at PT-1 in various substances.

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Conflict of interest

The author declares that he has no conflict of interest.

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