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Thermodynamics of substances with negative thermal expansion and negative compressibility

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ABSTRACT

It is shown that for substances with positive thermal expansion and positive compressibility, and for substances with negative thermal expansion and negative compressibility, $\delta Q = dU + PdV$, but for substances with positive thermal expansion and negative compressibility, and for substances with negative thermal expansion and positive compressibility, $\delta Q = dU - PdV$. The result obtained helps to calculate processes which do not obey traditional thermodynamics.

1. Introduction

According to thermodynamics [1],

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta}. \tag{1}$$

Here, S is the entropy, V is the volume, α is the thermal expansion coefficient, T is the temperature and β is the isothermal compressibility $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ where P is pressure. One can easily obtain this result:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V = \beta\left(\frac{\partial S}{\partial V}\right)_T. \tag{2}$$

From Eq. (1), when $\alpha < 0$, $\left(\frac{\partial S}{\partial V}\right)_T < 0$.

On the other hand,

$$\delta Q \le TdS = dU + PdV \tag{3}$$

and

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T} > 0. \tag{4}$$

for all α

However, $\left(\frac{\partial U}{\partial T}\right)_X \neq 0$, and generally $\left(\frac{\partial U}{\partial X}\right)_T \neq 0$ and $\frac{dU}{dT} = \left(\frac{\partial U}{\partial T}\right)_X + \left(\frac{\partial U}{\partial X}\right)_T \frac{dX}{dT} \neq 0$ where $X = P, V, S, H, F$ and G [1], H is the enthalpy, F is the Helmholtz free energy and G is the Gibbs free energy. Therefore, almost always, when U is constant then T is constant (as will be proven in detail below). When U is constant and T is constant then the right hand sides of Eqs. (1) and (4) must have the same sign. So, there is a contradiction in the thermodynamic equations. One has to pay attention that in a heat exchange, one introduces the quantity of heat δQ into the substance, and U and T vary. For this case, when U changes then T changes, and vice versa, thus when U is a constant then T is a constant, and vice versa. For some processes, of course, $\left(\frac{\partial U}{\partial V}\right)_T$ and $\left(\frac{\partial T}{\partial V}\right)_U$ are not equal to zero.

2. Theory

According to [1], $\left(\frac{\partial U}{\partial T}\right)_V = C_V$,

$$\left(\frac{\partial U}{\partial T}\right)_P = C_P - \alpha PV, \tag{5}$$

$$\left(\frac{\partial U}{\partial T}\right)_S = \frac{C_V \beta P}{\alpha T}, \tag{6}$$

$$\left(\frac{\partial U}{\partial T}\right)_H = \frac{C_P - \alpha PV - C_V \beta P}{1 - \alpha T}, \tag{7}$$

$$\left(\frac{\partial U}{\partial T}\right)_F = \frac{\beta SP - \alpha TS + C_V \beta P}{\beta P}, \tag{8}$$

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$$\left(\frac{\partial U}{\partial T}\right)_G = C_P - \alpha PV - (\alpha T - \beta P)S \tag{9}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T - \beta P}{\beta}, \tag{10}$$

$$\left(\frac{\partial U}{\partial P}\right)_T = (\beta P - \alpha T)V, \tag{11}$$

$$\left(\frac{\partial U}{\partial S}\right)_T = \frac{\alpha T - \beta P}{\alpha}, \tag{12}$$

$$\left(\frac{\partial U}{\partial H}\right)_T = \frac{\alpha T - \beta P}{\alpha T - 1}, \tag{13}$$

$$\left(\frac{\partial U}{\partial F}\right)_T = \frac{\beta P - \alpha T}{\beta P}, \tag{14}$$

$$\left(\frac{\partial U}{\partial G}\right)_T = \beta P - \alpha T. \tag{15}$$

So, in general $\frac{dU}{dT} = \left(\frac{\partial U}{\partial T}\right)_X + \left(\frac{\partial U}{\partial X}\right)_T \frac{dX}{dT}$ is not equal to 0. One can prove that for almost all processes, $\frac{dU}{dT} \neq 0$, thus when U is constant then T is constant and the contradiction does exist.

Let us find out what happens when U is constant but T is not constant [1]:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT + \frac{\alpha T - \beta P}{\beta} dV. \tag{16}$$

From this, if $\frac{dU}{dT} = 0$, then

$$\frac{1}{V}\frac{dV}{dT} = -\frac{\beta C_V}{(\beta P - \alpha T)V}. \tag{17}$$

For every process which does not satisfy Eq. (17), $\frac{dU}{dT} \neq 0$ and when U is constant then T is also constant.

For water at 273 K and atmospheric pressure, $\alpha = -68.05 \cdot 10^{-6}\ \mathrm{K}^{-1}$, $C_P = 4217.6$ J/(kgK), $C_P - C_V \approx 2.5$ J/(kgK) and $\beta = 5.09 \cdot 10^{-10}\ \mathrm{Pa}^{-1}$ [2]. Substituting these values into Eq. (17), one gets $\frac{1}{V}\frac{dV}{dT} = \frac{\beta C_V}{\alpha T V} \sim -0.1\ \mathrm{K}^{-1}$ with the highest accuracy. At a constant pressure, $\frac{1}{V}\frac{dV}{dT} = \alpha \approx -7 \cdot 10^{-5}\ \mathrm{K}^{-1}$, thus Eq. (17) is not true for water at a constant pressure. And, in general, for all processes with constant U and $\frac{1}{V}\frac{dV}{dT} \neq -0.1 \mathrm{K}^{-1}$, T is also constant.

From Eqs. (5) and (11) one can find that, when $\frac{dU}{dT} = 0$, then

$$\frac{dP}{dT} = \frac{C_P - \alpha PV}{(\alpha T - \beta P)V}. \tag{18}$$

For water, with the highest accuracy, $\frac{dP}{dT} = \frac{C_P}{\alpha T V} \sim -10^8$ Pa/K. For a constant pressure, $dP = 0$ hence Eq. (18) is wrong. For all processes with $\frac{dP}{dT} \neq -10^8 \mathrm{Pa/K}$, when U is constant then T is constant.

Another interesting example: recall that [1]

$$\left(\frac{\partial U}{\partial H}\right)_P = \frac{C_P - \alpha PV}{C_P}. \tag{19}$$

and

$$\left(\frac{\partial U}{\partial P}\right)_H = \frac{C_V \beta PV - (C_P - \alpha PV)V}{C_P}. \tag{20}$$

For water, with the highest accuracy, $\left(\frac{\partial U}{\partial H}\right)_P = 1$ and $\left(\frac{\partial U}{\partial P}\right)_H = -V$. Therefore, if $\frac{dU}{dT} = 0$, then

$$\frac{dP}{dH} = \frac{1}{V} = 10^3 \frac{\mathrm{Pa \cdot kg}}{\mathrm{m}^3}. \tag{21}$$

For heat exchange at constant pressure, $dH > 0$ but $dP = 0$ thus Eq. (21) is not true. In general, for all processes with $\frac{dP}{dH} \neq 10^3\ \mathrm{Pa \cdot kg/m^3}$, when U is constant then T is constant.

So, it is proven that for condensed matter in almost all cases, when U is a constant then T is a constant, and vice versa. This means, that for these cases

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta} = \left(\frac{\partial S}{\partial V}\right)_U. \tag{22}$$

(There is a general relation $\left(\frac{\partial S}{\partial V}\right)_U = \left(\frac{\partial S}{\partial V}\right)_T - \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T$ [1]). Using Eqs. (3), (4) and (22) one must come to the conclusion that for cases with $\alpha < 0$,

$$\delta Q \le TdS = dU - PdV \tag{23}$$

and

$$\frac{\alpha}{\beta} = \left(\frac{\partial S}{\partial V}\right)_U = -\frac{P}{T}. \tag{24}$$

The following consideration supports the conclusion made in this paper. There is the generalized Mayer's relation [3]:

$$C_P - C_V = \frac{T\alpha^2 V}{\beta}. \tag{25}$$

It is derived from the first and second laws of thermodynamics without simplification. Its derivation is given in the Appendix. If one derives it assuming that $TdS = dU - PdV$ for $\alpha < 0$, then it looks like [2]:

$$C_P - C_V = -\frac{T\alpha^2 V}{\beta} < 0. \tag{26}$$

Let us consider the thermal expansion of a solid. In the first approximation, V is constant. Then, in the first approximation [1],

$$C_P = \left(\frac{\partial H}{\partial T}\right)_V = C_V + \frac{\alpha V}{\beta}. \tag{27}$$

From Eq. (27), for $\alpha < 0$, $C_P < C_V$ and Eq. (26) is true, not Eq. (25).

In the second approximation, $P = \mathrm{const}$ and $V \neq \mathrm{const}$. Let us suppose that in that case $C_P > C_V$ for $\alpha < 0$. There is Rolle's lemma: If $f(x)$ is continuous in the interval $a \le x \le b$, and if $f(a) > 0$ and $f(b) < 0$ then there exists at least one value of x (say $x = c$) such that $f(c) = 0$, where $a < c < b$. As heat capacity is a continuous function, from Rolle's lemma it follows that there exists one value of V [say $V_c = V_0 + \Delta V$, V_0 is the constant V in Eq. (27)] such that $C_P(V_c) - C_V = 0$. This is a contradiction because from Eqs. (25) and (26), at $\alpha < 0$, $C_P(V) - C_V \neq 0$.

Else, when $P = \mathrm{const}$, for $V_0 - \Delta V < V < V_0 + \Delta V$ and $\alpha < 0$, due to the continuity of heat capacity, $C_P - C_V < 0$. This is another contradiction to