THERMODYNAMICS OF SUBSTANCES
WITH NEGATIVE THERMAL EXPANSION COEFFICIENT

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The 1st law of thermodynamics for heat exchange is \( dQ = dU + PdV \). According to Skornyakov (1995) *Tech. Phys. Lett.* 21(12) 949, there are no constraints for the conversion of heat into work, apart from the law of conservation of energy. Based on this result, in the present paper it has been shown that the 1st law of thermodynamics for substances with negative thermal expansion coefficient is the following one: \( dQ = dU - PdV \).

1. Introduction

The 1st law of thermodynamics for heat exchange has the following form:

\[
TdS = dU + PdV.
\]  
(1)

There are substances which contract with the temperature: water at 273<T<277 K, liquid He\(^4\), Si in a certain temperature interval, honey, Te, Se (monoclinic), quartz glass etc [1, 2]. Water contracts with the temperature at 273<T<277 K. Let’s carry out the process (1) with \( dU = 0 \) in this temperature interval: \( dQ > 0 \) and \( dV < 0 \). (In [3] is demonstrated a possibility of full conversion of heat to mechanical work: "This example provides the clearest evidence that the 2nd law of thermodynamics is untenable. There are no fundamental constraints for the conversion of heat into work, apart from the law of conservation of energy"). Throughout this paper pressure is supposed to be the atmospheric one. Then \( dQ = PdV \). It is a contradiction. Both sides of the equation have different signs. In this paper this paradox is explained.

2. Theory

It is possible to prove that at 273<T<277 K and \( dU = 0 \), water contracts with heating. From thermodynamics [1, 4]:

\[
\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V = k_T \left( \frac{\partial S}{\partial V} \right)_T,
\]  
(2)

where \( k_T \) is the isothermal compressibility. If \( \alpha < 0 \) then \( \left( \frac{\partial S}{\partial V} \right)_T < 0 \) and \( \left( \frac{\partial S}{\partial V} \right)_U < 0 \) because \( \left( \frac{\partial S}{\partial V} \right)_U \) is a special case of \( \left( \frac{\partial S}{\partial V} \right)_T \). From (1)

\[
\left( \frac{\partial S}{\partial V} \right)_T = \frac{P}{T} > 0.
\]  
(3)

Even, if it is impossible to carry out a process with \( dU = 0 \), one has to pay attention that chemical reaction never goes to the end, i.e. reactants never turn to products completely. Nevertheless, it is possible to calculate the whole heat of reaction exactly, it means, the heat of reaction where all reactants turn to the products (enthalpy \( \Delta H^0 \)). It is done by the Van't-Hoff equation, it is derived from the 1st and the 2nd law of thermodynamics without simplifications [5]:

\[
d/dT \ln K = \Delta H^0 / RT^2,
\]  
(4)
where $K$ is the reaction equilibrium constant. Thermodynamics must give opportunity to calculate the change of the volume $\Delta V$ for the process with $dU=0$ even if this process is impossible. For substances with the negative thermal expansion coefficient, the equation

$$dQ=dU+PdV$$  \hspace{1cm} (5)$$

will give wrong result. One has to arrive at a conclusion that for substances with negative $\alpha$, the sign before $P$ in (1) must be minus, but not plus:

$$dQ=dU-PdV.$$  \hspace{1cm} (6)$$

Whence $dQ=dQ_1+dQ_2$, $dQ_1=dU$, $dQ_2=\pm PdV$. If $dQ>0$ then $dQ_1>0$ and $dQ_2>0$.

Nobody has proved that for substances with the negative thermal expansion coefficient, $dQ_2$ must be less than 0 (when $dQ>0$). One sees that the 1st law of thermodynamics is not so irrefutable one supposed before. If even for one substance with negative $\alpha$, $dQ_2>0$ then it is already a sensation. The sense is the following one: one introduces the quantity of heat $dQ$ in the system and uses for that 100 kg fuel. 80 kg fuel is used for $dU$ and 20 kg is used for $PdV$. Another solution is: 120 kg for $dU$ and 20 kg for $PdV$. It has no physical sense.

Almost nobody checked experimentally validity of (1) for substances with $\alpha<0$. There are relations using which one can verify the 1st law [4, 6]: the Mayer's relation:

$$c_V-c_P=-T\alpha^2V/kT.$$  \hspace{1cm} (7)$$

The Reech's relation is

$$c_V=c_PkS/kT,$$  \hspace{1cm} (8)$$

where $k_S=(1/V)(\partial V/\partial P)_S$ is the adiabatic compressibility, and the relation

$$(\partial c_P/\partial P)_T=-TV((\partial \alpha/\partial T)_P+\alpha^2).$$  \hspace{1cm} (9)$$

If to derive these relations using (6) instead of (1), they will be the following ones:

$$c_V-c_P=TA^2V/kT,$$  \hspace{1cm} (10)$$

$$c_V=c_PkS/kT,$$  \hspace{1cm} (11)$$

$$(\partial c_P/\partial P)_T=TV((\partial \alpha/\partial T)_P+\alpha^2).$$  \hspace{1cm} (12)$$

For water at 273K $c_V-c_P=-2.5$ J/(kg·K), $c_P=4217.6$ J/(kg·K) [6]. Using (7) we can not verify the 1st law because we do not know $c_V$. We can do it using (8). For $T=273K$ $k_T=5.0885\times10^{-10}$ Pa$^{-1}$=$k_S$ [6]. These values can prove neither (1) nor (6).

The authors of [6] used the table dependence of enthalpy $H(P,T)$ from a reference book to obtain $(\partial c_P/\partial P)_T=\partial^2H/\partial P\partial T$. However, in reference books [7, 8] enthalpy is obtained from the relations

$$H=\Delta H_f^0+\int c_PdT,$$  \hspace{1cm} (13)$$

$$(\partial H/\partial P)_T=V-T(\partial V/\partial T)_P,$$  \hspace{1cm} (14)$$

where $\Delta H_f^0$ is the enthalpy of formation of substance and (9) is a sequence of (14). Hence, one may not agree with the result from [6] that $(\partial c_P/\partial P)_T>0$ in the whole temperature range.

Conclusions
The following conclusion can be drawn. It is very possible that (6) must be used instead of (1) for substances with negative thermal expansion coefficient. The final proof can be done by measuring precisely $c_v$, $k_f$, and $k_g$.

References


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