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The second maxwell relation must have a different sign

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ABSTRACT

It is shown that there is a mistake in the derivation of the second Maxwell relation. The mistake is corrected and the true relation is derived. One of its terms has another sign. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Maxwell relations;
Entropy;
Internal energy;
Thermodynamic derivatives;
Heat transfer.

INTRODUCTION

These are the first and second Maxwell relations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, \qquad (1)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad (2)$$

Here T, P, V, and S are the absolute temperature, pressure, volume, and entropy, respectively. The first one stems from the first law of thermodynamics:

$$\delta Q = T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V. \qquad (3)$$

Here δQ is the quantity of heat introduced into the system, and $\mathrm{d}U$ is the change in internal energy. It is shown that in the derivation of the second relation there is a mistake which, when corrected, changes the sign on the right-hand side of Eq. (2).

THEORY

Let us consider the traditional derivation of Eq.

(2)[1]. Introducing $\mathrm{d}U$ from Eq. (3) into the differential of enthalpy

$$\mathrm{d}H = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P \qquad (4)$$

we obtain:

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P. \qquad (5)$$

From Eq. (5), Eq. (2) results. However, $\mathrm{d}U$ from Eq. (3) is less than $\mathrm{d}U$ from Eq. (4) because in Eq. (3) it is for constant pressure, but in Eq. (4) it is for varying pressure. (One can argue in another way. If we introduce the same quantity of heat into the system in Eqs. (3) and (4), then $\mathrm{d}V$ in Eq. (4) is less than $\mathrm{d}V$ in Eq. (3), and the traditional derivation is not valid). The exact derivation must be as follows. In heat transfer with varying pressure, one introduces a quantity of heat into the system, and its internal energy, volume and pressure change:

$$\delta Q = T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P. \qquad (6)$$

We can rewrite the equation like this:

$$T\mathrm{d}S = T\mathrm{d}S_1 + T\mathrm{d}S_2 \qquad (7)$$

Where

$$\delta Q_1 = T\mathrm{d}S_1 = \mathrm{d}U_1 + P\mathrm{d}V \qquad (8)$$

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is the heat exchange at a constant pressure and leads to Eq. (1); and

$$\delta Q_2 = T dS_2 = dU_2 + V dP \tag{9}$$

is the heat exchange at a constant volume, and from it, omitting the subscripts, the second Maxwell relation is:

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_P. \tag{10}$$

We can see that it has a different sign on the right-hand side. Now Eqs. (1) and (10) look symmetric in relation to pressure and volume.

From Eqs. (8) and (9) it follows that the isochoric heat capacity, C_V, equals the isobaric heat capacity, C_P. In[2], the heat capacities of argon and nitrogen were measured experimentally, and it was found that $C_V = C_P$. Let us cite A. Guy[2]: "In a standard experiment in physical chemistry, students determine $C_P/C_V = 1.4$ for a diatomic gas such as nitrogen, but nowhere in the scientific literature is there a report on the direct experimental determination of both C_P and C_V for any gas."

Derivation of the second Maxwell relation by the Legendre transform does not change the result. One transforms the function $U(S,V)$ from Eq. (3) to the function $H(P,V)$ and gets Eq. (4). Then one introduces dU from Eq. (3) into Eq. (4).

CONCLUSIONS

It is proven that the previous derivation of the second Maxwell relation was wrong and the correct relation has been derived. It has a different sign in the right-hand term. The result obtained can have

an effect on the table of partial derivatives $\left(\dfrac{\partial Y}{\partial X}\right)_Z$

where X, Y, and Z are T, P, V, S, U, H, F and G (F and G are Helmholtz and Gibbs energies, respectively)[3].

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