NEW THERMODYNAMIC STATE FUNCTIONS

Andrei Rotaru*

abstract: In Thermodynamics, the Characteristic Functions Method represents a very important solving process. Thermodynamics demonstrates the existence of the characteristic functions, but cannot furnish their concrete form, which is possible only in Statistical Physics. Even without knowing their explicit form, there may be found important relations starting from the fact that they exist and they are state functions. This study proposes two new thermodynamic state functions $\pi_1$ and $\pi_2$, defined by the following equations: $\pi_1 = -\frac{U}{S}$ and $\pi_2 = -\frac{H}{S}$ and also interesting relations Temperature-Entropy and Volume-Pressure, through them, Massieu function and Planck function.

Introduction

The only two functions actually required in Thermodynamics are the internal energy $U$, obtained from the First Law of Thermodynamics, and the entropy $S$, obtained from the Second Law of Thermodynamics.

When the First and the Second Law are combined, the entropy function appears as an extensive independent variable.

It becomes convenient to define other functions, such as: Gibbs - $G$, Helmholtz - $F$, Massieu - $\Phi$, Planck – $\Psi$ and so on, for which the temperature, the volume, the pressure or the composition (if the system is open) are the independent variables, rather than the entropy.

The introduction of mass as an independent variable for the thermodynamic functions yields the equations that Gibbs called “fundamental”. It is on these equations that much of the development of the applications of Thermodynamics to chemical system is based on.

Many of the problems met in applications require the evaluation of various derivatives and the integration of differential quantities that involve the derivatives. If the derivatives are partial with respect to the extensive variables, they become intensive parameters [1].

So it is very important to find out a quick correlation between intensive and extensive variables, which is done through Legendre transformations [2]. Mathematically speaking, the thermodynamic functions – a fundamental one – $Z = Z (X_1, X_2 \ldots)$ or generally:

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should be substituted by a function:

\[ Z = Z(Y) \]  

(2)

where:

\[ Y = \frac{\partial Z}{\partial X} \]  

(3)

and represents the derivative of the function \( Z \) with respect to \( X \).

\[ Y = \frac{Z-W}{X-0} \]  

(4)

or: \( W = Z - XY \) where \( W \) is named Legendre transform of function \( Z \). The differential of the Legendre transform is:

\[ dW = dZ - XdY - YdX \]  

(5)

and because of (3):

\[ dW = -XdY \]  

(6)

or

\[ X = -\frac{\partial W}{\partial Y} \]  

(7)

These Legendre direct and reverse transforms are equivalent as can be seen from Table 1.

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If the Legendre transform is a function of only one variable \( W = Z(Y) \), then it is called a simple one; if it is a function of successive variables \( W = Z(Y_1, Y_2, \ldots) \), then it is called successive Legendre transform, i.e. \( G = H(T, P) \).

Therefore, after Legendre transformations, variables became functions and functions became variables [2].
Table 1. Direct and reverse Legendre transforms

<table>
<thead>
<tr>
<th>Function</th>
<th>Derivative</th>
<th>Transform</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z = Z(X)</td>
<td>Y = \frac{dZ}{dX}</td>
<td>W = Z - XY</td>
</tr>
<tr>
<td>W = W(Y)</td>
<td>-X = \frac{dW}{dY}</td>
<td>Z = W + XY</td>
</tr>
</tbody>
</table>

If one eliminates X and Z we have: W = W(Y)
If one eliminates W and Y we have: Z = Z(X)

There are a lot of state functions, not very often used in solving the problems of the Applied Thermodynamics, but very important for the correlation of the results of Statistical Physics with Thermodynamics [3].

In the Statistical Physics, in the study of one component system, one can use the Grand Canonical function, defined by: \( J = U(T, \mu) \), where \( J = U(T, \mu) = -PV \) with \( \frac{PV}{T} \) called Kramers function.

If we use \( S = S(U, V, N_1, \ldots) \) for defining other functions, we can obtain Massieu function [2-9]:

\[
S\left(\frac{1}{T}\right) = S - \frac{U}{T} = -\frac{F}{T} = \Phi \tag{8}
\]

or Planck one:

\[
S\left(\frac{1}{T}, \frac{P}{T}\right) = S - \frac{U}{T} - \frac{PV}{T} = S - \frac{H}{T} = -\frac{G}{T} = \Psi \tag{9}
\]

The Legendre transformations of entropy are:

\[
S(U, V) \rightarrow \Phi(T, V) \tag{10}
\]

\[
S(H, P) \rightarrow \Psi(T, P) \tag{11}
\]

Evolution and equilibrium criteria of general processes are expressed by the following relations [10]:

\[
(d\Phi)_{T,V} \geq 0 \tag{12}
\]

\[
(d\Psi)_{T,P} \geq 0 \tag{13}
\]

It is well known that these two state functions are not used very often.
Results and Discussion

In 1996, I. Petre proposed two new state functions \([6]\):

\[
\pi_1 = \pi_1(S,V) = -\frac{U}{S} = -T - \frac{F}{S}
\]

\[
\pi_2 = \pi_2(S,P) = -\frac{H}{S} = -T - \frac{G}{S}
\]

In this study we establish some of their properties, as well as interesting relations temperature-entropy and volume-pressure through them, Massieu function and Planck function.

First we must mention that they are Legendre transforms of temperature:

\[
T(F,V) \to \pi_1(S,V)
\]

\[
T(G,P) \to \pi_2(S,P)
\]

Table 2 contains the differential equations and the first order partial derivatives of Massieu function \(\Phi\), Planck function \(\Psi\) and of the new state functions \(\pi_1\) and \(\pi_2\).

<table>
<thead>
<tr>
<th>No</th>
<th>Thermodynamic state function</th>
<th>Variables</th>
<th>Differential equation</th>
<th>First order partial derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\Phi)</td>
<td>T,V</td>
<td>(\left(\frac{S-\Phi}{T}\right)dT + \frac{P}{T}dV)</td>
<td>(\frac{\partial \Phi}{\partial V}_T = \frac{S-\Phi}{T}, \frac{\partial \Phi}{\partial T}_V = \frac{P}{T})</td>
</tr>
<tr>
<td>2</td>
<td>(\Psi)</td>
<td>T,P</td>
<td>(\left(\frac{S-\Psi}{T}\right)dT - \frac{V}{T}dP)</td>
<td>(\frac{\partial \Psi}{\partial P}_T = \frac{S-\Psi}{T}, \frac{\partial \Psi}{\partial T}_P = -\frac{V}{T})</td>
</tr>
<tr>
<td>3</td>
<td>(\pi_1)</td>
<td>S,V</td>
<td>(-\left(\frac{T+\pi_1}{S}\right)dS + \frac{P}{S}dV)</td>
<td>(\frac{\partial \pi_1}{\partial V}_S = -\frac{T+\pi_1}{S}, \frac{\partial \pi_1}{\partial S}_V = \frac{P}{S})</td>
</tr>
<tr>
<td>4</td>
<td>(\pi_2)</td>
<td>S,P</td>
<td>(-\left(\frac{T+\pi_2}{S}\right)dS - \frac{V}{S}dP)</td>
<td>(\frac{\partial \pi_2}{\partial P}_S = -\frac{T+\pi_2}{S}, \frac{\partial \pi_2}{\partial S}_P = -\frac{V}{S})</td>
</tr>
</tbody>
</table>

These new thermodynamic state functions have the following properties:

1. they are Legendre transforms of temperature
2. \((d\pi_1)_S,V \geq 0\) and \((d\pi_2)_S,P \geq 0\)
3. the measure unit for these state functions is the temperature unit
4. the differential equations and first order partial derivatives are shown in Table 2
5. they are correlated whit the internal energy and the enthalpy

From the first order partial derivatives of Massieu and Planck state functions and equations \((8-9)\) there has been obtained:
\[ \Phi = \Psi - P \left( \frac{\partial \Psi}{\partial P} \right)_T \] (18)

\[ \Psi = \Phi - V \left( \frac{\partial \Phi}{\partial V} \right)_T \] (19)

If we compare eq. (18) with (19) we obtain:

\[ V \left( \frac{\partial \Phi}{\partial V} \right)_T = -P \left( \frac{\partial \Psi}{\partial P} \right)_T \] (20)

Table 2 is also used to obtain relations: \( \pi_1 - \pi_2 \), \( \pi_1 - \Phi \), \( \pi_2 - \Psi \).

The form of the relation between \( \pi_1 \) and \( \pi_2 \) can be obtained according to the sequences:

\[ U = H - PV = -S\pi_2 + PS \left( \frac{\partial \pi_2}{\partial P} \right)_S \] (21)

\[ U = S \left[ P \left( \frac{\partial \pi_2}{\partial P} \right)_S - \pi_2 \right] \] (22)

\[ \pi_1 = -\frac{U}{S} = -\left[ P \left( \frac{\partial \pi_2}{\partial P} \right)_S - \pi_2 \right] = \pi_2 - P \left( \frac{\partial \pi_2}{\partial P} \right)_S \] (23)

At the same time:

\[ H = U + PV = -S\pi_1 + VS \left( \frac{\partial \pi_1}{\partial V} \right)_S = S \left[ V \left( \frac{\partial \pi_1}{\partial V} \right)_S - \pi_1 \right] \] (24)

and

\[ \pi_2 = -\frac{H}{S} = -\frac{S \left[ V \left( \frac{\partial \pi_1}{\partial V} \right)_S - \pi_1 \right]}{S} = \pi_1 - V \left( \frac{\partial \pi_1}{\partial V} \right)_S \] (25)

If we compare \( \pi_1 \) and \( \pi_2 \) values from eq. (23) and eq. (25) we obtain:

\[ V \left( \frac{\partial \pi_1}{\partial V} \right)_S = -P \left( \frac{\partial \pi_2}{\partial P} \right)_S \] (26)

equation which provides the correlation \( \pi_1 - \pi_2 \).

The Helmholtz free energy can be calculated using eq.(22) and \( F = U - TS \):

\[ F = S \left[ P \left( \frac{\partial \pi_2}{\partial P} \right)_S + S \left( \frac{\partial \pi_2}{\partial S} \right)_P \right] \] (27)
At the same time: \( G = F + PV \) and \( V = -S\frac{\partial \pi_2}{\partial P} \) give the Gibbs free enthalpy:

\[
G = S^2\left(\frac{\partial \pi_2}{\partial S}\right)_P
\]  
(28)

A correlation between \( \Phi \) and \( \pi_1 \) can be easily obtained, first by finding the volume expression from eq. (19) and eq. (25):

\[
V = \frac{\Phi - \Psi}{\left(\frac{\partial \Phi}{\partial V}\right)_T}
\]  
(29)

\[
V = \pi_1 - \pi_2\left(\frac{\partial \pi_1}{\partial V}\right)_S
\]  
(30)

and then by comparing eq. (29) and eq. (30):

\[
\frac{\pi_1 - \pi_2}{\left(\frac{\partial \pi_1}{\partial V}\right)_S} = \frac{\Phi - \Psi}{\left(\frac{\partial \Phi}{\partial V}\right)_T}
\]  
(31)

\[
\pi_1\left(\frac{\partial \Phi}{\partial V}\right)_T - \pi_2\left(\frac{\partial \Phi}{\partial V}\right)_T = \Phi\left(\frac{\partial \pi_1}{\partial V}\right)_S - \Psi\left(\frac{\partial \pi_1}{\partial V}\right)_S
\]  
(32)

\[
\frac{U}{S}\left(\frac{\partial \Phi}{\partial V}\right)_T + \frac{H}{S}\left(\frac{\partial \Phi}{\partial V}\right)_T = -F\left(\frac{\partial \pi_1}{\partial V}\right)_S + G\left(\frac{\partial \pi_1}{\partial V}\right)_S
\]  
(33)

\[
\left(\frac{H - U}{S}\right)\left(\frac{\partial \Phi}{\partial V}\right)_T = \left(\frac{G - F}{T}\right)\left(\frac{\partial \pi_1}{\partial V}\right)_S
\]  
(34)

Equation (34) can be simplified through:

\[
U + G = H + F
\]  
(35)

resulting:

\[
T\left(\frac{\partial \Phi}{\partial V}\right)_T = S\left(\frac{\partial \pi_1}{\partial V}\right)_S
\]  
(36)

A correlation between \( \Psi \) and \( \pi_2 \) can be also obtained comparing:

\[
P = \frac{\pi_2 - \pi_1}{\left(\frac{\partial \pi_2}{\partial P}\right)_S}
\]  
(37)
\[ P = \frac{\Psi - \Phi}{\left( \frac{\partial \Psi}{\partial P} \right)_T} \]  

(38)

and then following the same sequences, one can find out that:

\[ T \left( \frac{\partial \Psi}{\partial P} \right)_T = S \left( \frac{\partial \pi_2}{\partial P} \right)_S \]  

(39)

If we divide rel.(20) by rel.(26) or rel.(36) by rel.(39) we will obtain:

\[ \left( \frac{\partial \Phi}{\partial V} \right)_T \left( \frac{\partial \pi_2}{\partial P} \right)_S = \left( \frac{\partial \Psi}{\partial P} \right)_T \left( \frac{\partial \pi_1}{\partial V} \right)_S \]  

(40)

Equations (20) and (26) represent the relation between Volume and Pressure, and equations (36) and (39) represent the relation between Temperature and Entropy.

Conclusions

Two new state functions and some of their properties were presented. We obtained four new equations, which can be used to find out correlation between the results of Statistical Physics and the principles of Thermodynamics. Without knowing the explicit form of theses characteristic functions, important relations such as temperature-entropy and volume-pressure have been deduced and also open the possibility to obtain new ones, based only on the fact that they are state functions.

REFERENCES