

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 π_1 and π_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 - Φ , Planck - Ψ 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 – $Z = Z(X_1, X_2 \dots)$ or generally:

* Faculty of Chemistry, Department of Physical Chemistry, University of Bucharest, 4-12 Regina Elisabeta, Bucharest, Romania

$$Z = Z(X) \quad (1)$$

should be substituted by a function:

$$Z = Z(Y) \quad (2)$$

where:

$$Y \equiv \frac{\partial Z}{\partial X} \quad (3)$$

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

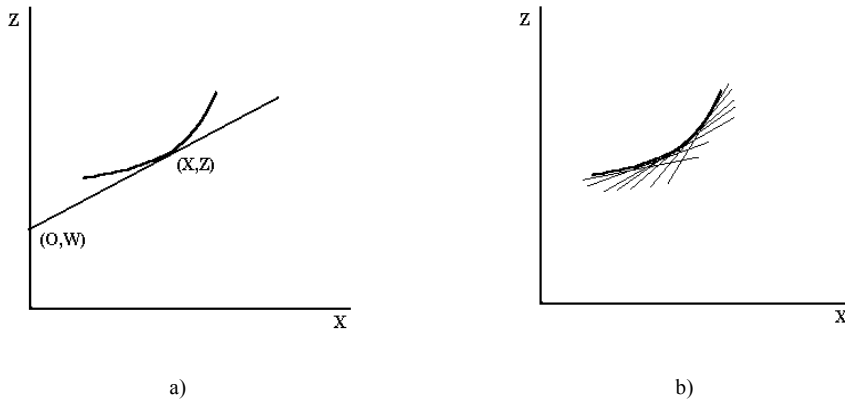


Fig. 1: $Z = Z(X)$ and the definition of the Legendre transform

Fig. 1(a,b). schematically shows the substitution of $Z = Z(X)$ by $Z = Z(Y)$. Also, one can calculate:

$$Y = \frac{Z - W}{X - 0} \quad (4)$$

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

$$dW = dZ - XdY - YdX \quad (5)$$

and because of (3):

$$dW = -XdY \quad (6)$$

or

$$X = -\frac{\partial W}{\partial Y} \quad (7)$$

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

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

Therefore, after Legendre transformations, variables became functions and functions became variables [2].

Table 1. Direct and reverse Legendre transforms

Function	$Z = Z(X)$	$W = W(Y)$
Derivative	$Y = \frac{dZ}{dX}$	$-X = \frac{dW}{dY}$
Transform	$W = Z - YX$	$Z = W + XY$
	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: $J \equiv U(T, \mu)$, where $J = U(T, \mu) = -PV$ with $\frac{PV}{T}$ called Kramers function.

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

$$S\left(\frac{1}{T}\right) = S - \frac{U}{T} = -\frac{F}{T} = \Phi \quad (8)$$

or Planck one:

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

The Legendre transformations of entropy are:

$$S(U, V) \rightarrow \Phi(T, V) \quad (10)$$

$$S(H, P) \rightarrow \Psi(T, P) \quad (11)$$

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

$$(d\Phi)_{T,V} \geq 0 \quad (12)$$

$$(d\Psi)_{T,P} \geq 0 \quad (13)$$

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]:

$$\pi_1 = \pi_1(S, V) = -\frac{U}{S} = -T - \frac{F}{S} \quad (14)$$

$$\pi_2 = \pi_2(S, P) = -\frac{H}{S} = -T - \frac{G}{S} \quad (15)$$

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:

$$T(F, V) \rightarrow \pi_1(S, V) \quad (16)$$

$$T(G, P) \rightarrow \pi_2(S, P) \quad (17)$$

Table 2. contains the differential equations and the first order partial derivatives of Massieu function Φ , Planck function Ψ and of the new state functions π_1 and π_2 .

Table 2. Differential equations and First order partial derivatives

No	Thermodynamic state function	Variables	Differential equation	First order partial derivatives
1	Φ	T, V	$\left(\frac{S-\Phi}{T}\right)dT + \frac{P}{T}dV$	$\left(\frac{\partial\Phi}{\partial T}\right)_V = \frac{S-\Phi}{T}, \left(\frac{\partial\Phi}{\partial V}\right)_T = \frac{P}{T}$
2	Ψ	T, P	$\left(\frac{S-\Psi}{T}\right)dT - \frac{V}{T}dP$	$\left(\frac{\partial\Psi}{\partial T}\right)_P = \frac{S-\Psi}{T}, \left(\frac{\partial\Psi}{\partial P}\right)_T = -\frac{V}{T}$
3	π_1	S, V	$-\left(\frac{T+\pi_1}{S}\right)dS + \frac{P}{S}dV$	$\left(\frac{\partial\pi_1}{\partial S}\right)_V = -\frac{T+\pi_1}{S}, \left(\frac{\partial\pi_1}{\partial V}\right)_S = \frac{P}{S}$
4	π_2	S, P	$-\left(\frac{T+\pi_2}{S}\right)dS - \frac{V}{S}dP$	$\left(\frac{\partial\pi_2}{\partial S}\right)_P = -\frac{T+\pi_2}{S}, \left(\frac{\partial\pi_2}{\partial P}\right)_S = -\frac{V}{S}$

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:

$$\Phi = \Psi - P \left(\frac{\partial \Psi}{\partial P} \right)_T \quad (18)$$

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

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

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

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

The form of the relation between π_1 and π_2 can be obtained according to the sequences:

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

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

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

At the same time:

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

and

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

If we compare π_1 and π_2 values from eq. (23) and eq. (25) we obtain:

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

equation which provides the correlation $\pi_1 - \pi_2$.

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

$$F = S \left[P \left(\frac{\partial \pi_2}{\partial P} \right)_S + S \left(\frac{\partial \pi_2}{\partial S} \right)_P \right] \quad (27)$$

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

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

A correlation between Φ and π_1 can be easily obtained, first by finding the volume expression from eq. (19) and eq. (25):

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

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

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

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

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

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

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

Equation (34) can be simplified through:

$$U + G = H + F \quad (35)$$

resulting:

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

A correlation between Ψ and π_2 can be also obtained comparing:

$$P = \frac{\pi_2 - \pi_1}{\left(\frac{\partial \pi_2}{\partial P} \right)_S} \quad (37)$$

$$P = \frac{\Psi - \Phi}{\left(\frac{\partial \Psi}{\partial P}\right)_T} \quad (38)$$

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

$$T \left(\frac{\partial \Psi}{\partial P}\right)_T = S \left(\frac{\partial \pi_2}{\partial P}\right)_S \quad (39)$$

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

$$\left(\frac{\partial \Phi}{\partial V}\right)_T \left(\frac{\partial \pi_2}{\partial P}\right)_S = \left(\frac{\partial \Psi}{\partial P}\right)_T \left(\frac{\partial \pi_1}{\partial V}\right)_S \quad (40)$$

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 these 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

1. Cenuse, Z. (2004) **Chemical Thermodynamics**, Ed. Universitatii Bucuresti, Bucuresti.
2. Sandulescu, D. (1979) **Chimie fizica**, Ed. Stiintifica si Enciclopedica, Bucuresti.
3. Lungu, P.R. (2003) **Termodinamica**, Ed. Universitatii Bucuresti, Bucuresti.
4. Wood, S.E. and Battino, R. (1990) **Thermodynamics of Chemical Systems**, Cambridge University Press, New York
5. Klotz, I.M. (1994) **Chemical Thermodynamics**, Wiley-Interscience Publication, John Wiley and Sons Inc., New York.
6. Petre, I. and Anitescu, G. (1996) **Fizica Moleculara, I Elemente de Termodinamica**, Ed. Universitatii Bucuresti, Bucuresti.
7. Ciobanu, G., Gherman, O. and Saliu, L. (1983) **Fizica Moleculara, Termodinamica si Statistica**, Ed. Didactica si Pedagogica, Bucuresti.
8. Moisil, G. (1988) **Termodinamica**, Ed. Academiei R. S. Romania, Bucuresti.
9. Gábos, Z. and Gherman, O. (1964) **Termodinamica si Fizica Statistica**, Ed. Didactica si Pedagogica, Bucuresti
10. Vilcu, R. (1994) **Termodinamica Chimica**, Editura Tehnica, Bucuresti.